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WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

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No. 2041.—JANUARY 6, 1899.

RADIUM: A NEW BODY, STRONGLY RADIO-ACTIVE, CONTAINED IN PITCHBLENDE.

By M. P. CURIE, Mdme. P. CURIE, and M. G. BÉMONT.

Two of us have shown that, by purely chemical processes, a strongly radio-active substance can be extracted from pitchblende. This substance is near bismuth in its analytical properties. We therefore came to the conclusion that pitchblende might contain a new element, for which we proposed the name of Polonium (*Comptes Rendus*, vol. cxxvii., p. 175; CHEMICAL NEWS, vol. lxxviii., p. 49).

Our subsequent researches are in accord with the results first obtained, but concurrently with these we have met with a second substance, strongly radio-active, and entirely differing from the first body in its chemical properties.

Polonium is precipitated from its solution by sulphuretted hydrogen. Its salts are soluble in acids, and are precipitated by water; polonium is completely precipitated by ammonia. The new radio-active substance we have discovered has, to all appearance, the properties of almost pure barium. It is not precipitated either by sulphuretted hydrogen nor by ammonium sulphide, nor by ammonia; its sulphate is insoluble in water and acids; the carbonate is insoluble in water; the chloride is very soluble in water, but insoluble in concentrated hydrochloric acid and in alcohol. It gives the barium spectrum easy to recognise. Nevertheless we believe this substance, although in greater part consisting of barium, contains besides a new element which gives to it radio-activity, and which is close to barium in its chemical properties.

Here are the reasons which lead us to this opinion:—

1. Barium and its compounds are not radio-active; also one of us has shown that radio-activity appears to be an atomic property, persisting through all the chemical and physical states of the substance. From this point of view the radio-activity of our substance, not being due to barium, should be attributed to another element.

2. The first substances we obtained had, in the state of hydrated chloride, an activity sixty times as great as that of metallic uranium (the radio-activity was measured by the amount of conductivity conferred on air in our apparatus). On dissolving these chlorides in water and precipitating a portion by alcohol, the part precipitated is much more active than the part left in solution. Taking advantage of this fact we may, by a series of fractionations, obtain chlorides more and more active. We have thus obtained chlorides having an activity 900 times greater than that of uranium. We were stopped here by failure of material, but from the progress of the operations we could see that the activity would have augmented still more had we been able to continue. These facts may be explained by the presence of a radio-active element, the chloride of which is less soluble in alcoholised water than is that of barium.

3. M. Demarçay has been good enough to examine the spectrum of our substance. The results are given in a note following this. M. Demarçay has found in its spectrum a ray which does not appear to be due to any known element. This ray, scarcely visible with the chloride sixty times more active than uranium, is notable with the chloride concentrated by fractionation to an activity 900 times than that of uranium. The intensity of this ray augments, therefore, with the radio-activity, and this we think is a very serious reason for attributing it to the radio-active portion of our substance.

These different reasons lead us to believe that the new radio-active substance contains a new element, to which we propose to give the name of radium.

We have determined the atomic weight of our active barium by estimating the chlorine in the anhydrous chloride. We have found numbers differing very little from those obtained with inactive barium chloride; however, the numbers for the active barium are always a little higher, but the difference is of the order of magnitude of experimental errors. The new substance certainly contains a very large proportion of barium; in spite of this its radio-activity is considerable. The radio-activity of radium ought therefore to be enormous.

Uranium, thorium, polonium, and radium, and their compounds, render air a conductor of electricity, and act photographically on sensitive plates. From these points of view polonium and radium are considerably more active than uranium and thorium. On photographic plates we obtain good impressions with radium and polonium in half a minute; it requires several hours to obtain the same result with uranium and thorium.

The rays emitted by compounds of polonium and radium render barium platinocyanide fluorescent; their action in this respect is analogous to that of the Röntgen rays, but is considerably more feeble. To make the experiment place on the active substance a very thin sheet of aluminium, and on this a thin layer of barium platinocyanide; in the dark the barium platinocyanide appears feebly luminous over the active substance.

We thus realise a source of light, very faint, it is true, but functioning without a source ef onergy. There is here a contradiction, at least apparent, to the principle of Carnot.

Uranium and thorium under the same circumstances give no light, their action probably being too feeble. —*Comptes Rendus*, vol. cxxvii., p. 1215, Dec. 26, 1898.

ON THE

ANALYSIS OF MOLYBDENUM COMPOUNDS.

By HARRY BREARLEY.

(Continued from vol. lxxviii., p. 205).

II. Separations from Molybdenum.

In this Section we propose to take some elements whose presence interferes with the estimation of molybdenum as lead molybdate when carried out in the ordinary way, although, as will be seen later, it is not always necessary to previously separate such elements.

The adoption of a reagent for separatory purposes obliges us to establish, first, that such reagent itself does not interfere with the estimation of molybdenum, and, secondly, the separation effected by it is at least reasonably accurate. The first consideration at once vetoes a number of processes which admirably answer to the requirements of the second. The obviation of this difficulty, by in turn separating the excess of the first reagent by a less objectionable one, has been disregarded on the ground that such a complication of processes would make the estimation of molybdenum as lead molybdate inferior to its estimation by other means.

Sulphuric Acid.

From the fact that molybdenum occurs in Nature very largely as a sulphide (molybdenite) the interference of sulphuric acid is an important one; it is important also from the fact that as a reagent it forms a number of insoluble sulphates. The estimation of molybdenum in its presence would be falsified by a simultaneous formation of sulphate and molybdate of lead. Theoretically, a resort to ammonium acetate, in which lead sulphate is soluble, should remedy the error, and experiment shows that practicable amounts of acetate can retain very considerable amounts of lead sulphate in solution when no other metal is being precipitated.

Where a separation depends on the presence of a subsidiary reagent whose object it is to prevent the co-precipitation of an objectionable compound, then the *order* in which the operations are performed is frequently a matter of some moment. Thus in the case before us we may avail ourselves of the qualities of ammonium acetate by adding it to the mixture of molybdic and sulphuric acids, or by adding it to the lead acetate, and then, for either way, we may pour into the mixed acids or into the lead acetate. In all, then, there are four ways in which the precipitation of the lead molybdate may be performed, and three of them invariably have given high results. The fourth way has always given very accurate results, and its order is as follows:—Heat to boiling the solution of molybdic and sulphuric acids (part of the H_2SO_4 may be present as free acid), and to an amount of lead acetate more than sufficient to precipitate the molybdenum add, say, 30 c.c. of strong ammonium acetate; heat this also, and then pour *the second mixture into the first;* bring the whole to boiling, filter, &c.

Some results are—

20	50 c.c. normal H_2SO_4 present.
0·1000	0·1001
0·0998	0·1000
0·1000	
0·1001	

The precipitates were tested, in each case, for sulphuric acid, with negative results.

Barium, Strontium, and Calcium.

Having established a procedure under which sulphuric acid is innoxious, it remains to enquire whether the precipitation of barium, calcium, and strontium, as sulphates, is an accurate means of separating these elements from molybdenum.

Barium readily forms a molybdate in a neutral or even a slightly acidified (acetic) solution. Indeed the precipitation from neutral or slightly ammoniacal solutions is quantitatively exact for pure molybdates at any rate. To prevent this reaction complicating the precipitation of the barium sulphate, a small quantity of hydrochloric acid—in which $BaMoO_4$ is easily soluble—is added, and then with an excess of sulphuric acid, not needlessly large, the barium is precipitated from a boiling solution.

After ignition the barium sulphate is never perfectly white; it has, particularly when cold, a slight green tinge. If the precipitated $BaSO_4$ be kept boiling for ten or twenty minutes, the tinge is somewhat fainter. If it is caused by associated molybdenum the amount present must, even in the worst cases, have been practically negligible. On purifying the ignited $BaSO_4$, by re-dissolving in strong sulphuric acid and subsequently diluting, the green tinge is always observable in the moist precipitate; but after ignition the precipitate is perfectly white, and its weight hardly differs from the first.

The molybdenum in the filtrate is estimated with the afore-mentioned precautions respecting H_2SO_4.

Test Analyses.

0·1	0·2 grm. Ba present.
0·1001	0·1005 Mo recovered.

Calcium and Strontium.

These two elements are not so completely precipitated as insoluble sulphates as is barium. Happily, however, there are circumstances under which they need not be removed at all, and consequently no trouble was taken to use the various accessories—alcohol, &c.—of a complete precipitation.

Both calcium and strontium form molybdates in neutral solutions. These molybdates are less and less readily formed as the amount of free acetic acid in the solution is increased. Their behaviour in this respect is in the Ba, Sr, Ca order, barium being decidedly the most refractory. When solutions of 200 c.c. contain one or two tenths of a grm. of Ba, Ca, and Sr, along with about 20 c.c. of acetic acid, the molybdates can be formed, even on long-continued boiling, only with barium. On this property of the alkaline earths is based a method of estimating molybdenum in their presence.

Here, as in the presence of sulphuric acid, it is important to add the reagents in a certain order. If to the faintly acid (HCl) solution of molybdenum and strontium (say) there be added ammonium acetate, acetic acid, and lead acetate, in the order stated, the results are invariably 2 or 3 per cent too low, presumably on account of an admixture of the less weighty molybdates of Sr. By dissolving the ignited precipitate in hydrochloric acid, and re-precipitating under like conditions, the error is amended.

The much more accurate way is to add a few c.c. of HCl in excess, then acetic acid and lead acetate. Unless too much HCl has been added, the molybdenum is partially precipitated at this stage; the addition of ammonium acetate completes it. Up to the addition of lead acetate the solution should have been kept at boiling-point; after adding the ammonium acetate the filtration may be proceeded with without further heating. For the sake of brevity I shall subsequently refer to this as the "acid precipitation."*

* The precipitated lead molybdate has at no time been very difficult to filter, but with the acid precipitation it comes down almost sand-like. The filtration of a single sample through paper-pulp is as much as one can comfortably attend to.

Test Analyses.

	0·1	0·2 grm. added element.
Strontium	0·1001	0·1000
Calcium	0·0997	0·0997

In the application of this procedure to barium it is particularly necessary to avoid boiling after the precipitation is complete, and even so with the same amount of reagents as were used for calcium and strontium the results were from 1 to 2 per cent too low with one precipitation. This is less to be regretted since barium is so completely separated with sulphuric acid.

Extended Application of the Acid Preparation.

I now found that a number of elements which on preliminary trial had been passed over, as needing to be separated, could easily be disposed of by the acid precipitation, and I am of opinion that if this form of precipitation along with pump filters had been adopted for those elements previously tabulated (Chem. News, lxxviii, 203) there would have been no cause to call attention to the contamination of the lead molybdate with traces even of cobalt, manganese, or nickel.

The test analyses of a number of further elements treated in this way are collected in—

Table II.

Metal added.	0·1	0·2 grm. added.
Arsenic	0·0999	0·1001
Cadmium.. ..	0·1000	0·1000
Aluminium ..	0·1003	0·0999
Uranium	—	0·1002

The arsenic, used as potassium arsenite, forms a precipitate with the lead salt even in acetic solutions. This precipitate is not formed if the solution be moderately acidified with nitric or hydrochloric acid, and then the other reagents added in the previously named order.

Uranium was included in Table I. The results of the ordinary precipitation were, however, admittedly unsatisfactory even after re-precipitation. The acid titration furnishes much better results, and, should a re-precipitation be deemed necessary, a more effective way is to dissolve the ignited precipitate in a small excess of soda hydrate in the manner explained below (see Chromium).

Soda Silicate.

As a number of molybdenum compounds can be most readily decomposed by alkaline fusion, silicate of soda frequently obtrudes itself on the analyst's notice. If present in very large amounts the acid solution gelatinises it, and renders any practicable filtration of the lead molybdate impossible. After dehydrating the silica by evaporating the acid (HCl) solution to dryness and baking, the molybdenum is completely re-dissolved by boiling with dilute hydrochloric acid, and is thus separated.

The evaporation is frequently a very slow process. We find it more expeditious and quite practicable with amounts up to half a grm. silica to acidify the solution with HCl and boil. In this way some silica may be precipitated, but it is usually in such a state as does not retard the filtration. After boiling for several minutes the precipitation is completed as usual. It might be thought that simply to re-dissolve the ignited precipitate, and filter off any silica which may have been precipitated, would enable one to correct the result; but such is not the case. It is necessary to re-precipitate the solution after filtering. The following test analyses show results calculated—I. before separating silica, II. after deducting silica, and III. after re-precipitation.

I.	II.	III.	SiO_2 (present as potass. silicate.
0·1015	0·1010	0·1001	0·1 grm.
0·1014	0·1008	0·1002	0·2 ,,
0·1033	0·1007	0·1000	0·3 ,,

Iron.

It is the combinations of iron and molybdenum which most frequently come to my notice, and great pains were therefore taken to precipitate the molybdenum without a preliminary separation of the iron. So far all attempts have been unsuccessful. The compound which molybdenum forms with iron in neutral and nearly neutral solutions is not to be lightly disposed of. It behaves very persistently like the basic chromate of iron, which has been previously shown (Chemical News, lxxvii., p. 49) to falsify a great many analytical schemes.

As the iron had to be separated, a mixture of the two metals was prepared and its free acid determined. Equal amounts of this mixture, containing 0·1 grm. of molybdenum and 0·2 grm. of iron, were precipitated with varying excesses of alkali of two normal strength and raised to boiling. The figures given are the amounts of molybdenum recovered from the filtrate:—

Table III.

Alkali used	0	10	30	50 c.c. excess used.
Ammonia hydrate	0·0329	0·0732	0·0849	0·0890
Soda carbonate..	—	0·0936	0·0997	0·0998
Soda hydrate ..	—	0·1000	0·1002	0·1003

The precipitation of iron as basic acetate is perfectly useless as a means of separating iron and molybdenum. The recovery increases with the acetate, but 50 c.c. strong ammonia acetate added to a portion of the solution just used separated only 30 per cent of the molybdenum, and it is possible to arrange a separation so that hardly any molybdenum shall be separated at all. This point is worthy of remark, as there are occasions when it is desirable to have the iron and molybdenum precipitated together. It seems also very probable that alkaline molybdates could be very successfully used like the corresponding chromates (Chemical News, lxxviii., 14), for replacing the acetates in the separation of iron from other members of its own group.

As this process applied to the details of the analysis of steel and steel-making alloys would too greatly interfere with the consideration of other separations, the subject is being treated in a separate paper.

Chromium.

So far as available references go, I find that the customary way of separating molybdenum and chromium is to precipitate the latter element with ammonia. De Benneville, who applies this procedure to the analysis of some molybdenum chromium irons (*Jour. Iron and Steel Inst.*, 1895, 205 and 229), finds that it is necessary to re-dissolve and re-precipitate the chromic hydrate, and also to boil for at least half an hour after adding the ammonia. The former precaution I can quite confirm, and even after that it is easy to imagine that the separation is not perfect, or approximately so. The need for the latter precaution I have not experienced. There is always, of course, the need to boil for a little while so as to re-precipitate the dissolved chromic hydrate, even when solutions of pure chromic salts are being dealt with, but that the precipitation in presence of molybdenum constitutes a special case, and may go astray through the formation of $Cr_2(Mo_2O_7)_33(NH_4)_2Mo_2O_720H_2O$ compounds seems to rest on somewhat slender evidence. However, the point is not an important one since the separation, however performed, is very unsatisfactory. The following test analyses show the effect of using increasing amounts of ammonia:—

5 c.c.	20 c.c.	30 c.c. $2N.NH_4HO$ in excess.
0·0591	0·0715	0·0785 Mo recovered.

A separation with as little as 10 c.c. of 2N soda hydrate in excess seems to be a very approximately accurate one. If the soda hydrate is added to the cold solution the chromic hydroxide is re-dissolved, but re-precipitated on boiling. If added to the boiling solution the precipitation

takes place at once, but is never, in either case, *quite* complete, however long the solution be boiled. A little of the chromium, more so if precipitated from cold solutions than otherwise, is always converted into sodium chromate, and is wholly precipitated along with the molybdenum as lead chromate, the condition of precipitation being equally favourable to either acid. This unfortunate interference decreases with the excess of soda used, but as the excess must always exceed a minimum, the error cannot be altogether eliminated if the amount of chromium to be separated is at all considerable.

The most satisfactory procedure is as follows. Nearly neutralise the acid solution of molybdenum and chromium, heat to boiling, and then add an excess of soda hydrate; or if the chromium present is several times larger in amount than the molybdenum, add the mixture to the soda with constant shaking. Boil for about ten minutes, filter off an aliquot portion, acidify, and precipitate the Mo. Both the moist and the ignited $PbMoO_4$ may have a yellow or even an orange colour. Re-dissolve in HCl, add dilute soda hydrate to the heated solution until the precipitate, once formed, just re-dissolves, boil, filter, wash, and from filtrate re-precipitate the lead molybdate after adding a little more lead acetate. The latter precipitate should be only faintly tinted yellow. Some idea of the colouring power of lead chromate may be obtained by observing the decided yellow precipitate, which is separated from a solution in which the dichromate colour is hardly discernible. Test analyses :—

5	10	20 c.c. 2N.NaHO excess.
0·0962	0·1000	0·0993 Mo recovered.

Attempts have been made to reduce the small amounts of CrO_3 so that they might be removed in one operation with the chromic hydrate. A great number of reducing agents are inactive to soda chromate in alkaline (soda) solutions, and such as are active introduce a greater error than they obviate by causing some of the molybdenum to be also precipitated.

An attempt made to precipitate molybdenum from a solution of chromic chloride in the cold showed that if lead acetate were added to a slightly acidified (HCl) solution, and then ammonium acetate, the lead molybdate comes down as a beautiful lustrous precipitate, and on continuing to add the acetate is re-dissolved. The heated solution turns milky, and on nearing boiling point deposits a dense faintly green precipitate. The circumstance of its formation suggests that this precipitate may be a definite compound. So far, however, no quantitative analysis has been made. This precipitate, after boiling for some ten or fifteen minutes, contains the whole of the molybdenum, and when ignited has generally a grey colour.

In adopting this way of analysing a chrome molybdenum compound, the ordinary acid precipitation is followed until the ignited grey precipitate is obtained. This is then boiled with hydrochloric acid, and ignoring a dark coloured insoluble powder (Cr_2O_3), the lead molybdate is re-precipitated and re-dissolved in soda hydrate as previously described. This is a more expeditious means of analysing chrome-molybdenums than any other I have tried. Test analyses :—

0·1	0·2 grm. Cr added.
0·1005	0·1002 Mo recovered.

The "acid precipitation," which has been so conspicuously successful and reliable under widely varying circumstances, may be advantageously adopted for estimating Mo in solutions of pure alkaline molybdates. Its chief recommendation is the fact that the form of the precipitate is more conducive to rapid filtering and washing. In the moist state its colour is more distinctly creamy than when precipitated in the usual way, and this creaminess might unwittingly be mistaken for evidence of chromate. After ignition, however, the precipitate has the usual colour of pure $PbMoO_4$.

Phosphoric Acid.

The estimation of molybdenum as lead molybdate in presence of salts of this acid at once suggests difficulties, due either to the formation of lead phosphate or of phosphomolybdates. The first of these compounds is by far the more formidable, and has occasioned more trouble than any other body dealt with.

Adrian and Trillat (*Journ. de Pharm. de Chim.*, vol. vii., No. 11; Chemical News, lxxviii., 255) point out that phosphoglycerates are distinguished from neutral and acid phosphates by—amongst other things—the solubility of its lead salt in acetic acid. An attempt was made to utilise this feature as a means of holding the phosphoric acid in solution. This it is easily possible to do, so long as only salts of lead and phosphorus are present, but the precipitation of molybdenum invariably disturbed the equilibrium, and carried down large amounts of lead phosphate.

The want of success with this method is to be ascribed to ignorance of the precise conditions under which this property of phosphoglycerates can be successfully taken advantage of rather than to any inherent impossibility. When an interfering element has to be eliminated in the above way, nothing short of a thorough examination of every possible way of performing the operation can support the conclusion that the elimination is impossible. Such great care became unnecessary by the opening of a new and more promising course. It is well, however, to put on record the fact that lead molybdate may be accurately precipitated from solutions containing large amounts of glycerine.

On applying the "acid precipitation" to a solution containing 2 or 3 decigrms. of soda phosphate it was found that about 80 per cent of the phosphate had passed into solution. This appears to be chiefly due to the fact that acid phosphate of lead ($PbHPO_4$) is soluble in ammonia chloride. On re-dissolving the ignited precipitate and destroying the free HCl with ammonia acetate, the formation of the lead molybdate is preceded by the yellow phosphomolybdate. This interference is visible if there is the least delay during the addition of the acetate, and is probably present in a degree however the acetate be added.

Already there was evidence that here we were dealing with one of those cases in which the order of performing the operation was of great importance. This much can usually be surmised from the results of an experiment in which the estimated element is added last. Thus, here, to the clear solution containing soda phosphate, lead acetate, ammonia chloride, and the excess of ammonium acetate used to decompose the HCl, there was added 1 decigrm. of Mo. The result was less than 2 per cent too high. This order, of course, cannot possibly be imitated in practice, but the experiment usually fixes the high water mark of precision obtainable in any other way.

The plan finally adopted was to add to the solution containing the Mo and P salts enough HCl to prevent the formation of a precipitate on the subsequent addition of more than enough lead acetate to combine with the molybdic and phosphoric acids as $PbMoO_4$ and $PbHPO_4$ respectively.* This heated solution is then poured into another hot solution containing more than enough ammonium acetate to decompose the HCl, and from 10 to 15 grms. of ammonium chloride. The lower flask, which is violently shaken during the operation and for a little while afterwards, is digested for a few minutes and the solution filtered. The filtrate must be tested for excess of lead acetate by adding a drop of molybdate solution. The reverse order, addition of more lead acetate, always leads to a precipitate if much phosphate was originally present. Prolonged boiling of the clear filtrate may also lead to a precipitate if the acid lead phosphate was present in

* The more desirable way—addition of HCl to dissolve the combined precipitates of phosphate and molybdate—leads to the formation of phosphomolybdates in the hot, and is interfered with by the formation of lead chloride in the cold solution.

greater amount than could be comfortably dissolved by the ammonium salts, but I have never found such a precipitate to contain more than the merest traces of molybdenum. The precipitate is the most easily filtrable of any yet met. Indeed it was desirable, in order to get a head of wash water, to use a funnel with a constricted stem.

The ignited precipitate may or may not contain phosphorus according to the amount originally present. With 0·3 grm. of soda phosphate along with 0·1 grm. of molybdenum, the first precipitate calculated to Mo gave, in two separate cases, 0·1060 grm. If such considerable amounts of phosphorus are being dealt with, the precipitation must be repeated by simply dissolving in HCl, and adding as before to a mixture of ammonium acetate and chloride. The same two precipitates after this operation gave 0·1000 and 0·0996 grm. of Mo respectively. A similar estimation in a solution containing 0·6 grm. of soda phosphate gave 0·1003 grm. of molybdenum.

These precipitates may be tested for phosphates by dissolving in hydrochloric acid and gently adding dilute ammonia. Just before lead molybdate would form, if more ammonia were added, the yellow phosphomolybdates will form if phosphates are present, or ammonia may be straightway added in excess and the precipitate carefully re-dissolved in nitric acid.

Where the lead phosphate present amounts only to 1 or 2 per cent of the weight of the ignited precipitate, it has been found to be very approximately accurate to complete the precipitation of the phosphomolybdate by shaking, filter through pulp, ignite, and from the formula $P_2O_5(Mo_6O_{17})_4$, containing 1·75 per cent P, to calculate the P to $Pb_3(PO_4)_2$ and subtract from the weighed $PbMoO_4$.

(To be continued).

A CHLORO-IODIDE OF TIN.

By C. LENORMAND.

In a preceding communication I have already mentioned, among the compounds formed by a metal united at the same time with several halogen elements, the existence of a new chlorobromide,—that is to say, a chlorobromide of iron. I now describe another of these compounds, a chloro-iodide of tin, obtained by the action of iodine on anhydrous protochloride of tin.

Iodine, at the normal temperature, has no very sensible action on anhydrous protochloride of tin; but at the same time crystals of iodine placed in contact with this salt gradually disappear, and we notice a coloured product form, which gradually gives the surface of the protochloride a bright red hue.

If a mixture of iodine and anhydrous chloride of tin in excess is heated in an open tube over a gas flame, an energetic reaction takes place; the iodine disappears and one portion of the mass becomes liquid, while abundant yellow fumes escape into the atmosphere. Finally the unattacked protochloride remains as residue.

If we conduct the operation, as I did in the case of ferric chlorobromide, in sealed tubes at 100°, the reaction is less vigorous and less rapid, but is complete at the end of a few hours,—above all, if we take care to shake up the tubes from time to time, so as to bring the unattacked chloride into contact with the remaining iodide. On cooling, a bright red, mobile, and dense liquid is found in the tubes, in which the excess of protochloride of tin, necessary to use, is found: this can be separated by decantation.

Analysis shows that the liquid thus obtained is a chloro-iodide of tin.

For estimating the tin in this body I did not use M. Ladenburg's method by which he obtained the chlorobromide $SnCl_2Br_2$, nor that of M. Classen, which consists in determining the tin by the electrolytic method. I was able to work in a more simple manner by taking advantage of the action of water on this substance. When thrown into water, in fact, this latter causes a precipitate, which dissolves gradually, but more quickly on agitation. The diluted solution is decomposed by heat; even at 65° all the tin is found to be precipitated in the state of gelatinous stannic hydrate, at the same time the iodine and the chlorine remain in solution in the form of hydriodic and hydrochloric acids. I weighed the tin as stannic oxide, this being obtained by the estimation of the precipitated hydrate. The chlorine and iodine were weighed by Rose's method. The following are the results:

	Calculated. $SnCl_2I_2$.	Found.		
Tin	26·63	26·78	26·50	26·77
Chlorine.. ..	16·00	15·84	15·91	15·91
Iodine	57·37	57·31	54·48	57·29
	100·00	99·93	99·89	99·97

This compound corresponds with the formula $SnCl_2I_2$, —that is, a chloro-iodide of tin.

This body is a bright red and very mobile liquid, giving off abundant yellowish fumes, but still fuming less than does stannic chloride. Its density at 15° is 3·287. When poured into a small quantity of water it gives off a considerable quantity of heat, forming a certain hydrate which we propose to examine later on, and which is soluble in an excess of water. If poured into ether chloro-iodide of tin gives rise to the formation of an insoluble compound, accompanied by a rise of temperature. Ethylic, propylic, butylic, and amylic alcohols cause the same phenomena, crystallised compounds being formed. It is soluble in benzene, sulphide of carbon, and chloroform.

Heat has a curious action on chloro-iodide of tin; when heated the liquid commences to distil over at 191°; after this the temperature can be increased without any change, and a wine-red liquid comes over. At about 297° the temperature does not increase and distillation stops.

If the residue and the distilled liquid be analysed, we find the stannic iodide in the retort, and in the recipient a mixture of three elements—viz., tin, chlorine, and iodine—containing all the chlorine of the original chloro-iodide.

The actual figures were, for 100 grms. distilled, 55·44 grms. found in the residue, and 44·55 grms. in the distilled liquid.

The analysis of the 55·44 grms. of residue gave as result:—

	Calculated for 55·44 per cent SnI_4.	Found.			Mean.
Tin	10·45	10·25	10·38	10·36	10·33
Iodine ..	44·98	44·94	44·87	44·99	44·93
Chlorine ..	0·00	0·00	0·00	0·00	0·00
	55·43	55·19	55·25	55·35	55·26

Thus the residue found in the retort corresponds well with the formula SnI_4 of stannic iodide.

The analysis of the 44·55 grms. of the distilled liquor was as follows:—

				Mean.
Tin	16·62	16·54	16·59	16·58
Iodine ..	12·43	12·40	12·35	12·39
Chlorine..	15·58	15·67	15·79	15·68
	44·63	44·61	44·73	44·65

If we add together the tin, the iodine, and the chlorine of these two analyses, we arrive at the following results:—

	Residue.	Distillate.	Total.
Tin	10·33	16·58	26·91
Iodine	44·93	12·39	57·32
Chlorine	0·00	15·68	15·68
			99·91

from which it is at once seen that all the chlorine contained in the 100 grms of the original chloro-iodide passed over in the distillation. But this is not all.

If the 44·55 grms. of the distilled liquor be submitted to a fresh distillation, it can be seen that boiling does not occur until the temperature reaches 140°, and that the temperature continues to rise until it becomes stationary at about 297°, while stannic iodide, SnI_4, still remains in the retort.

On further distillation an analogous phenomenon takes place, but the boiling-point goes down to 124° the while the distillation proceeds, the temperature again stops at about 297°, and we again find stannic iodide, SnI_4, in the retort.

This operation may be carried out a third and a fourth time, and the same results will be found, but the quantities of SnI_4 gradually decrease as the boiling-point becomes less.

Finally, on the fifth rectification, the substance only boils at 116°, and the retort contains only stannic iodide, while the liquid distilled contains all the chlorine which was first combined in the state of stannic chloride.

In 100 parts of $SnCl_2I_2$ originally distilled I found in the fifth distillation an amount of chloride of tin equal to 26·82, while 14·26 was the quantity of chlorine present.

The decomposition should take place according to the equation $2(SnCl_2I_2) = SnCl_4 + SnI_4$. In fact, for 100 grms. of $SnCl_2I_2$ we get theoretically 70·6 grms. of SnI_4 and 29·4 of $SnCl_4$.

Now, I have found after my repeated rectifications 67·78 of SnI_4 and 26·82 of $SnCl_4$, numbers which are sufficiently close to theory, *i.e.*, 70·6 and 29·4. I say *close*, inasmuch as during the five successive distillations a certain quantity of the liquid distilled is bound to be lost.

As I have already said, the final decomposition takes place according to the formula already given, but it cannot now be said what formulæ govern the intermediate reactions. Stannic iodide is left as a residue at each distillation; this substance is not volatile at the temperatures at which I have worked: how, then, can the iodine pass over by distillation? It seems probable that we must admit the existence of an intermediate dissociable and volatile chloro-iodide of tin. In any case this point seems to have a certain amount of interest, and I hope soon to forward a further communication.—*Journ. de Pharm. et de Chim.*, 1898, Series 6, vol. viii., No. 6.

DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.*

By J. MERRITT MATTHEWS.

1. Introduction.

The tetrachlorides of several of the members of Group IV. have been studied in their deportment with certain organic nitriles and amines, and the results seem to indicate that there is a general tendency toward reactions between these tetrachlorides and the latter-named reagents, giving rise to definitely constituted compounds. That is to say, the tetrachlorides of Group IV. appear to possess an acidic character in their ability to combine with certain organic bases to form neutral salts. This behaviour has already been studied with reference to the tetrachlorides of carbon, silicon, titanium, and tin; and although the data at our command are neither as connected nor as complete as might be desired, nevertheless, they may be regarded as sufficient to establish a characteristic group reaction. In these reactions, however, there appear to be several unaccountable fluctuations and divergences among the different members of the group. It would be natural to expect a difference in the behaviour of the metallic sub-group including germanium, tin, and lead, from the more non-metallic sub-group including titanium, zirconium, and thorium. But such a conclusion does not appear to receive the necessary strength from the actual facts observed in order to give it a sure foundation; for titanium seems to exhibit a greater analogy in its reactions to those of tin than to any other. The number of reactions studied, however, have been so few that it would be presumptuous to formulate a comprehensive law regarding the general reactions of the two sub-groups in question, and in consequence of their being no such law established, it would be illogical to argue that apparently diverging reactions pointed necessarily to inconsistencies in the behaviour of the two sub-groups.

The tetrachlorides of silicon, titanium, and tin have been rather comprehensively studied in their behaviour toward nitriles and amines. Titanium tetrachloride has been found to be reactive with formonitrile, acetonitrile, benzonitrile, toluonitrile, succinonitrile, chlorcyanogen, sulphur monochloride, phosphorus pentachloride, and the vapours of aqua regia. The tetrachloride of tin also exhibits analogous reactions with every one of the above mentioned reagents; silicon tetrachloride, however, shows no evidence of reacting with these compounds.

All three of these tetrachlorides give derivatives with ammonia and aromatic amines, as does also carbon tetrachloride. With the fatty amines, however, only the chlorides of silicon and tin have been found to be reactive.

2. Preparation of the Tetrachlorides of Zirconium, Thorium, and Lead.

A. *Zirconium Tetrachloride.*

The zirconium tetrachloride used in this research was prepared in the following manner:—Carefully selected crystals of zircon were finely powdered and fused with acid potassium sulphate; the fusion was lixiviated with water and filtered; the residue was dried and fused with potassium hydroxide in a nickel dish. This fusion, after being digested with water and filtered, left a white amorphous residue of zirconium dioxide. The oxide was mixed with pulverised starch and molasses to a thick batter, which was then rolled into small pellets about 1 c.m. in diameter. These were slowly dried in an air oven until all moisture was expelled, when they were transferred to a covered silver crucible and charred until no more vapours were evolved. These pellets, containing zirconium dioxide intimately mixed with pure charcoal, were placed in a long glass combustion tube, and strongly heated in a current of dry chlorine gas. Zirconium tetrachloride was formed by this procedure, and collected in the cooler part of the tube in the form of a white powder or minute crystals. The salt thus obtained was dissolved in ether which had been carefully dehydrated by repeated distillation over sodium, until thin slices of the metal remained untarnished on being in contact with the ether for several days. The zirconium tetrachloride in the form of this ethereal solution was used in all the experiments, as it gave a convenient and uniform method for testing the reactions.

B. *Thorium Tetrachloride.*

This salt was prepared in a manner precisely analogous to that given for zirconium. The dioxide, ThO_2, was obtained from a quantity of the nitrate which was available for the purpose by precipitation with ammonium hydroxide and subsequent ignition. The tetrachloride was dissolved in dehydrated ether, as in the case of the zirconium salt, and this solution was used in all of the reactions.

C. *Lead Tetrachloride.*

This compound was prepared by the method of Friedrich (*Ber. d. Chem. Ges.*, xxvi., 1434). One part of lead chloride was suspended in twenty parts of concentrated hydrochloric acid, and a current of chlorine gas was conducted

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx., No. 11. From author's thesis for the Degree of Doctor of Philosophy.

hrough the liquid until nearly all of the lead dichloride had gone into solution, which required about twenty hours. The temperature of the liquid during the entire process was kept at about 4° C. by means of a freezing mixture. The yellow-coloured liquid which resulted from this treatment consisted of a solution of lead tetrachloride in concentrated hydrochloric acid. Two parts of ammonium chloride dissolved in ten parts of water were then added, and a bright lemon-yellow crystalline precipitate was produced, consisting of the ammonium double salt of lead tetrachloride, which, according to Friedrich, has the formula $PbCl_4 \cdot 2NH_4Cl$. Classen and Zahorski (*Ztschr. Anal. Chem.*, iv., 100), however, apparently obtain the same salt—by practically the same method—and they ascribe to it the formula $2PbCl_4 \cdot 5NH_4Cl$. The ammonium double salt was filtered off and washed free from hydrochloric acid and chlorine with absolute alcohol and ether. A portion of this salt was placed in a separatory funnel and digested with fuming sulphuric acid of specific gravity 1·879. A brisk reaction took place, and yellow oily drops of lead tetrachloride soon separated out; these were washed by decantation several times with fuming sulphuric acid, and finally dissolved in chloroform which had been carefully dehydrated over fuming sulphuric acid. This chloroform solution of the lead tetrachloride was used for all the reactions; but fresh portions and solutions had to be made for each experiment, as the tetrachloride decomposed into the lower chloride in a few hours. It was found impossible to work with the liquid tetrachloride itself, as it was immediately decomposed on coming in contact with the air, and even decomposed in about twelve hours when kept under fuming sulphuric acid. The strength of the acid used for the decomposition of the ammonium double salt is an important factor in this preparation, as an acid of less strength than that used above will fail to give the lead tetrachloride in any appreciable quantity.

3. The Action of Nitriles, &c., on the Tetrachlorides.

As zirconium occupies the next position to titanium in the same sub-group, it was natural to suppose that its tetrachloride would exhibit reactions with the nitriles somewhat analogous to those of the latter element, and that the analogy might also be followed into the fatty and aromatic amines. Contemporary with this present work there was carried to completion in this same laboratory a study of the reactions of silicon tetrachloride; and as both tin and titanium have been studied in this same connection, it was considered that a research into the possible derivatives of the allied members of this group might lead to results which would be useful in establishing analogies and comparisons between the different members of Group IV., as viewed from their respective behaviour with the reagents used in this study. By this means it was thought probable that a definite law might be formulated for the group with regard to these reactions, and that the heterogeneous data, heretofore lying dissociated and useless, might be brought together and systematically understood.

a. Vapours of Aqua Regia.—The dry vapours of aqua regia conducted into the solution of zirconium tetrachloride gave no reaction, the solution only becoming discoloured by the gases, which were again liberated on raising the temperature. Portions of the dry zirconium salt were also placed in a porcelain boat, and heated in a current of the dry vapours of aqua regia; but the salt appeared to volatilise unchanged, and no compound was formed. In this behaviour zirconium shows a deviation from that of titanium, as the tetrachloride of the latter reacts readily with the vapours of aqua regia, giving a compound corresponding to the formula $3TiCl_4 \cdot 2NO_2Cl$, Hampe (*Ann. Chem., Liebig*, cxxvi., 43). An analogous compound with tin tetrachloride has been prepared by the same investigator. Baeyer (*Ber. d. Chem. Ges.*, vii., 1639) also records the compound $SnCl_4 \cdot 2NOCl$.

The solutions of the tetrachlorides of thorium and lead behaved similarly to that of zirconium, and gave no derivatives.

b. Nitrogen Dioxide.—This gas, obtained by heating lead nitrate, on being conducted into the solutions of the tetrachlorides, gave no reaction beyond a simple solution of the gas. The dry salts of zirconium and thorium, heated in a current of the gas, volatilised unchanged and gave no compound.

c. Sulphur Monochloride.—On mixing this substance with the solutions of the tetrachlorides no reaction was observed.

d. Chlorides of Phosphorus.—The action of both the tri- and pentachlorides of phosphorus was tried on the solutions of the tetrachlorides, but no combination resulted.

e. Dicyanogen.—On conducting this gas into the solutions of the tetrachlorides no reaction took place; nor does it seem to have formed any compounds with the corresponding salts of titanium or tin.

f. Formonitrile.—Though both titanium and tin tetrachlorides give derivatives with hydrocyanic acid, yet no product was obtained by allowing this compound to act on the three tetrachlorides here investigated.

g. Cyanogen Chloride.—It was prepared by the action of chlorine on mercuric cyanide, but it gave no reactions with the solutions of the tetrachlorides.

h. Acetonitrile.—The vapours of this nitrile passed into the solutions of the tetrachlorides yielded no compounds, although derivatives have been obtained with the titanium and tin salts.

i. Benzonitrile.—Like acetonitrile, this aromatic body yielded no derivatives with the tetrachlorides.

Summary.

From these experiments it is to be observed that the nitriles and the other reagents here used, which for the most part gave additive compounds with the tetrachlorides of titanium and tin, are without action on the corresponding salts of zirconium, thorium, and lead.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 15th, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Stuart Blofeld, 4, Camden Gardens, West Kensington Park, W.; Bertram H. Bowles, 53, Dunsmure Road, Stamford Hill, N.; Thomas John Cheater, 6, Boutflower Road, Wandsworth Common, S.W.; George Ward Hedley, 2, St. Luke's Villas, Cheltenham; Harold Octavius Knight, Westfield Villa, Barton-on-Humber; Dudley Northall-Laurie, 56A, Pall Mall, S.W.; James McCracken, 580, Govan Road, Govan, N.B.; John O'Sullivan, 742, Nicola Street, Vancouver City, B.C.; Arthur Lee White, 29, Huron Road, Upper Tooting, S.W.

Mr. H. P. Bell was formally admitted a Fellow of the Society.

The following papers were read:—

147. "*The Interaction of Ethylic Sodiomalonate and Mesityl Oxide.*" By Arthur W. Crossley.

Attempts to prepare dihydrocamphoric acid synthetically have so far proved unsuccessful (*Trans.*, 1898, lxxiii., 23). Isobutylene dibromide does not condense with ethylic sodiomethylmalonate, nor mesityl oxide with ethylic sodiomalonate, in the expected manner. The thick, oily product obtained in the latter case cannot be distilled in a

vacuum without partial decomposition; when hydrolysed with alcoholic potash it yields a dibasic *acid*, $C_{16}H_{24}O_4$, which crystallises from acetone in colourless, transparent, lustrous prisms belonging to the monosymmetric system, and melts at 148—148·5°, the upper part of the capillary tube becoming covered with a red film. The *ethylic* salt separates from light petroleum in thick, transparent, lustrous prisms, which usually are twinned, and apparently belong to the monosymmetric system. It melts at 59·5—60°, boils at 252° in air without decomposition, and, on hydrolysis, yields the original acid. The *silver* salt crystallises from water in feathery needles.

Sodium amalgam is without action on the acid. Bromine readily converts it into a *dibromo*-derivative, $C_{16}H_{24}O_4Br_2$ or $C_{16}H_{22}O_4Br_2$, which crystallises from dilute alcohol in colourless, glistening leaflets containing $2H_2O$, and melts with slight decomposition at 171°. On treatment with hydrogen bromide, a *dihydrobromide*, $C_{16}H_{26}O_4Br_2$, is obtained, which crystallises in transparent prisms, melts at 169° with decomposition, and is re-converted into the acid, $C_{16}H_{24}O_4$, by interaction with alcoholic potash.

The acid is readily oxidised by alkaline potassium permanganate in the cold, and when the product is treated with chromic acid an acid melting at 89° is obtained. It is hoped that a study of its oxidation products will give some clue to the constitution of the substance.

148. "*The Interaction of Ethylic Malonate and Acetylene Tetrabromide in presence of Sodium Ethoxide.*" By ARTHUR W. CROSSLEY.

This investigation was undertaken in the hope that ethylic disodiomalonate and acetylene tetrabromide would interact according to the equation,—

$$C_2H_2Br_4+2Na_2C(CO_2Et)_2=$$
$$=(CO_2Et)_2C{:}CH{\cdot}CH{:}C(CO_2Et)_2+4NaBr,$$

as the product, on hydrolysis and subsequent heating, should yield muconic acid, $CO_2H{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$, from which tetrabromadipic acid could be prepared for the purpose of investigating its behaviour with weak alkalis.

The reaction does not take place as expected, and is of a complicated nature, the two main products being tribromethylene, $CHBr{:}CBr_2$, and tetrethylic acetylenetetracarboxylate; during its progress acetylene is given off, and tarry products are also formed from which no definite chemical compound could be isolated.

The acetylene tetrabromide used was prepared from acetylene generated from calcium carbide by the action of water, and purified by Willgerodt's method (*Ber.*, 1895, xxviii., 2108). It boiled at 151° under 54 m.m. pressure, and was a clear, colourless, highly refractive liquid.

0·1548 gave 0·3353 AgBr. Br=92·18.
$C_2H_2Br_4$ requires Br=92·48 per cent.

Acetylene tetrabromide (1 mol.) was added to a mixture of sodium (2 mols.) dissolved in absolute alcohol and ethylic malonate (2 mols.), and after the violent reaction had somewhat moderated, the whole was heated on a water bath for 1½ hours. Water was added to the resulting dark, reddish green, feebly-acid product, and the whole extracted with ether. On washing the ethereal extract with water, the greater portion of the red colouring matter (from which the tarry products alluded to were obtained) was removed, and also a small quantity of a green solid containing sodium and organic matter. When boiled with acids this green substance partially dissolved, forming a red solution, which was again turned green by addition of an alkali; but the amount was too small for investigation. On distilling the residue from the dried ethereal extract, fractions were obtained boiling at 65—80° and at 225—230° under 47 m.m. pressure, and not more than 0·5 c.c. passed over between these limits.

The fraction boiling at 65—80° under 47 m.m. pressure contained tribromethylene, $CHBr{:}CBr_2$. This clear, colourless, heavy liquid, amounting to 63 per cent of the total ethereal extract, was repeatedly fractionated at the ordinary pressure, and nearly the whole passed over between 164—166°; the residue, when heated above this temperature, gave off bromine and hydrogen bromide, and consisted probably of some unchanged acetylene tetrabromide. On analysis the fraction boiling at 164—166° gave the following numbers:—

0·3410 gave 0·7251 AgBr. Br=90·47.
$CHBr{:}CBr_2$ requires Br=90·56 per cent.

The substance was further characterised by converting it into pentabromethane by the direct addition of bromine. The resulting solid crystallised from alcohol in long, white, glistening needles melting at 55—55·5°.

0·2656 gave 0·5887 AgBr. Br=94·31.
$CHBr_2{\cdot}CBr_3$ requires Br=94·11 per cent.

The fraction boiling at 225—230° under 47 m.m. pressure contained tetrethylic acetylenetetracarboxylate. This fraction solidified almost completely. It was spread on a porous plate, and then purified by re-crystallisation from light petroleum boiling at 60—80°, from which it separated in long, white, silken needles melting at 75—76°.

0·1518 gave 0·2936 CO_2 and 0·0940 H_2O. C=52·76; H=6·87.
$(CO_2Et)_2CH{\cdot}CH(CO_2Et)_2$ requires C=52·83, H=6·91 per cent.

Although the conditions under which the reaction was carried out were varied to some extent, the same results were always obtained.

149. "*Derivatives of Camphoric Acid.*" Part III. By F. STANLEY KIPPING, D.Sc., F.R.S.

This paper contains an account of the preparation, properties, and transformations of a number of compounds which have been obtained from π-bromocamphoric acid, and is a continuation of previous work (*Trans.*, 1896, lxix., 913; Kipping and Pope, *Trans.*, 1897, lxxi., 963).

πw-Dibromocamphoric acid, πw-dibromocamphoric anhydride, and π-bromocamphanic acid have been already briefly described (*Proc.*, 1895, xi., 211).

$w\pi$-Chlorobromocamphoric anhydride,—

$$C_8H_{12}ClBr\begin{matrix}CO\\CO\end{matrix}>O,$$

is obtained by treating π-bromocamphoric acid with phosphorus pentachloride, and then passing chlorine into the product heated at 100°. It crystallises in large, orthorhombic prisms melting at 214—215°, and resembles the corresponding dibromo-compound in ordinary properties.

$w\pi$-Chlorobromocamphoric acid, $C_8H_{12}ClBr(CO_2H)_2$, can be prepared by heating its anhydride with concentrated nitric acid; it is a colourless, crystalline compound melting at about 197°, and is very like the dibromo-acid in all respects.

When $w\pi$-chlorobromocamphoric anhydride is boiled with dilute acetic acid it is converted into a π-bromocamphanic acid, identical with the compound melting at 176—177°, obtained by the decomposition of πw-dibromocamphoric anhydride.

Methylic π-bromocamphanate,—

$$CO_2Me{\cdot}C_8H_{12}Br\begin{matrix}CO\\|\\O\end{matrix},$$

is easily obtained from the corresponding acid by the ordinary methods; it crystallises in orthorhombic prisms, melts at 87—88°, and dissolves freely in most of the ordinary organic solvents.

π-Bromocamphanamide,—

$$NH_2{\cdot}CO{\cdot}C_8H_{12}Br\begin{matrix}CO\\|\\O\end{matrix},$$

is produced when πw-dibromocamphoric anhydride is left in contact with aqueous ammonia, and can also be prepared from methylic π-bromocamphanate in a similar

manner; it crystallises in transparent needles melting at 161—162°.

The action of alkalis on *πw*-dibromocamphoric anhydride results in the formation of hydroxy-*cis* *π*-camphanic acid (*Trans.*, 1896, lxix., 913), but when the anhydride is heated with an aqueous solution of silver nitrate, it is partly converted into the *γ*-lactone of hydroxycamphotricarboxylic acid (*loc. cit.*); the last-named compound is also formed when *π*-bromocamphanic acid is boiled with an aqueous solution of silver nitrate.

150. "*Synthesis of αββ-Trimethylglutaric Acid.*" By W. H. Perkin, jun., and J. F. Thorpe.

This acid, which is especially interesting on account of the fact that Balbiano (*Ber.*, 1895, xxviii., 2161) obtained it by simple reactions from camphoric acid, may be prepared synthetically in the following way.

Ethylic cyanacetate is digested in alcoholic solution with sodium ethylate and ethylic dimethylacrylate, and the product, which contains the sodium compound of *ethylic α-cyano-ββ-dimethylglutarate*,—

$$CO_2Et(CN)CNa{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2Et,$$

is treated with methylic iodide. The resulting *ethylic α-cyano-αββ-trimethylglutarate*,—

$$CO_2Et(CN)CMe{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2Et,$$

a colourless oil boiling at 181° under 25 m.m. pressure, yields on hydrolysis *αββ-trimethylglutarimide*,

$$CMe_2\begin{matrix}CH_2-CO\\CHMe{\cdot}CO\end{matrix}NH,$$

which crystallises in long needles and melts at 126°.

αββ-Trimethylglutaric acid,—

$$CO_2H{\cdot}CHMe{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

is obtained from this imide by heating with hydrochloric acid at 200°; it melts at 88°, gives an *anhydride* melting at 82°, and an *anilic acid* melting at 150°, and is, in all its properties, identical with the acid obtained from camphoric acid by Balbiano.

151. "*Hydrolysis of Methylic and Ethylic γ-Cyanoacetoacetates and their Derivatives.*" Part I. By W. Trevor Lawrence.

A preliminary account is given of the results obtained in an investigation which had, for its primary object, the preparation of unsymmetrically disubstituted ethylic acetonedicarboxylates, but has led to the discovery of a new series of acids.

Methylic γ-cyanodimethylacetoacetate,—

$$CN{\cdot}CH_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Me,$$

is the chief product of the interaction of methylic *γ*-bromodimethylacetoacetate with potassium cyanide in ethereal solution. It boils at 126—128° under 18 m.m. pressure. On treatment in ethylic alcohol solution with dry hydrogen chloride it yields an oil,—

$$CO_2Et{\cdot}CHCl{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et,$$

which boils at 146—150° under 40 m.m. pressure, and when hydrolysed with concentrated hydrochloric acid is converted into *αα*-dimethyl-*β*-hydroxyglutaconic acid. Sodium amalgam does not reduce the nitrile under the varied conditions employed, but converts it into dimethylmalonic acid.

Methylic *γ*-cyanodimethylacetoacetate is hydrolysed rapidly by concentrated hydrochloric acid, and converted quantitatively into a substance which is regarded provisionally as *αα-dimethyl-β-hydroxyglutaconic acid*,—

$$CO_2H{\cdot}CH{:}C(OH){\cdot}CMe_2{\cdot}CO_2H,$$

although several of its reactions are difficult to explain if the formula adopted is correct. Thus, the compound remains unchanged on boiling with sulphuric and with nitric acids, is not affected by potassium permanganate at 60°, and gives no colouration with ferric chloride. The acid crystallises from water in prisms, melts at 214°, and distils at 245°. The *hydrogen silver* salt, $C_7H_9O_5Ag$, and the corresponding *copper* and *zinc* salts have been obtained. The *aniline* salt melts at 122°. The *dimethylic* salt, $CO_2Me{\cdot}CH{:}C(OH){\cdot}CMe_2{\cdot}CO_2Me$, crystallises in needles, melts at 104°, and boils at 285°. The *acetyl* derivative melts at 136°, and the *benzoyl* derivative at 208°. When the acid is treated with phosphorus pentabromide and the product poured into methylic alcohol, the methylic salt of a bromo-derivative is obtained which, on hydrolysis with hydrobromic acid, yields *αα*-dimethylglutaconic acid.

αα-Dimethylglutaconic acid,—

$$CO_2H{\cdot}CH{:}CH{\cdot}CMe_2{\cdot}CO_2H,$$

is also obtained by the reduction of dimethylhydroxyglutaconic acid with hydriodic acid at 130° in sealed tubes. It crystallises from water in prisms, melts at 148, and is not reduced by sodium amalgam in the cold.

The following compounds have also been prepared:—

Ethylic γ-bromomethylethylacetoacetate,—

$$CH_2Br{\cdot}CO{\cdot}CMeEt{\cdot}CO_2Et,$$

boiling at 164° under 75 m.m. pressure; *ethylic γ-cyanomethylethylacetoacetate*,—

$$CN{\cdot}CH_2{\cdot}CO{\cdot}CMeEt{\cdot}CO_2Et,$$

boiling at 158° under 35 m.m.; *αα-methylethyl-β-hydroxyglutaconic acid*, $CO_2H{\cdot}CH{:}C(OH){\cdot}CMeEt{\cdot}CO_2H$, melting at 164°; *ethylic γ-bromodiethylacetoacetate*,—

$$CH_2Br{\cdot}CO{\cdot}CEt_2{\cdot}CO_2Et,$$

boiling at 180° under 100 m.m. pressure; *ethylic γ cyanodiethylacetoacetate*, $CN{\cdot}CH_2{\cdot}CO{\cdot}CEt_2{\cdot}CO_2Et$, boiling at 158° under 75 m.m. pressure; *αα-diethyl-β-hydroxyglutaconic acid*, $CO_2H{\cdot}CH{:}C(OH){\cdot}CEt_2{\cdot}CO_2H$, melting at 159°.

Different results are obtained by the hydrolysis of these nitriles by means of sulphuric acid and of methyl alcoholic potash; moreover, the products of the reduction of the hydroxyglutaconic acids with hydriodic acid differ with the conditions. The author is engaged in investigating these reactions, as well as the behaviour of the *γ*-nitriles of ethylic acetoacetate and its derivatives generally.

NOTICES OF BOOKS.

Commercial Organic Analysis. A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, &c., with Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By Alfred H. Allen, F.I.C, F.C.S., Past President of the Society of Public Analysts, Public Analyst for the West Riding of Yorkshire, the City of Sheffield, &c. Second Edition, Revised and Enlarged. Vol. IV.—Proteids and Albuminous Principles. London: J. and A. Churchill, 7, Great Marlborough Street.

With this volume Mr. Allen's extensive work is brought to a conclusion, its production having extended over fourteen years. The work is worthy of the author, and has already proved of great value to the profession.

In the Preface to this volume Mr. Allen regrets that he is unable to personally undertake the thorough revision of the earlier part of the work as he had originally intended, but proposes to publish an Appendix to each volume which shall include the more important facts that have accumulated during recent years. The partial revision of the earlier volumes is being undertaken by Dr. Henry Leffmann, of Philadelphia, and vol. I. is already published, while vol. II. will follow shortly.

Much of the matter in the present volume is of special practical interest, being the outcome of the author's analytical experience. Through the kindness of Dr. T.

E. Thorpe, the Government method for analysing milk has been included in full detail; there is also a very complete article on the absorption spectra of hæmoglobin and its allies, followed by a full description of the spectroscopes and micro-spectroscopes used, with practical hints on their manipulation.

At the end of the book will be found Addenda to many of the articles, giving details of papers by different authors, bearing on subjects that have appeared in various journals up to the present date.

Throughout the work the high standard of excellence that characterised the first volume has been maintained.

Matter, Energy, Force, and Work. By Silas W. Holman. London and New York: The Macmillan Company.

This is a well thought out and carefully written treatise on the fundamental ideas of Physical Science. There is nothing absolutely novel in the book, yet as a whole it is a distinct advance on any work of its class that we have come across.

The author takes energy as his starting point, and shows that force and work, both internal and external, are functions of it. Further, starting from the demand of the kinetic theory of gases for a complex atom, and from the necessity of the idea of space being filled with something known as ether, he shows how the vortex-atom, so far as it has been mathematically investigated, fulfils both demands, and at the same time leaves energy in its position as the one unchangeable and indestructible function.

We can recommend this work to our readers as being well worth reading.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

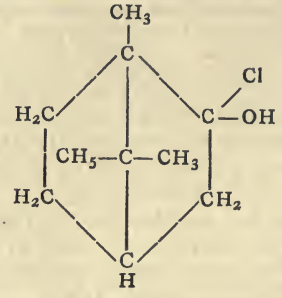
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 16, October 17, 1898.

A New Hydrate of Chromium.—G. Baugé.—This new oxide of chromium is capable of several stages of hydration. (1), $Cr_3O_4.H_2O$, obtained already by Peligot. (2), $Cr_3O_4.3H_2O$, a brownish yellow hydrate, which the author prepares very rapidly by closing one of the ends of the tube containing the brick-red hydrate mentioned below. The tube is then placed in boiling water, and the air pumped out until the hydrate loses some of its water. This substance is comparatively stable. (3), a brick-red unstable hydrate, of which the author's analyses have led him to suppose contains four molecules of water.

Action of Soda Ammonium on Arsenic.—C. Hugol.—The author, when acting upon phosphorus with soda ammonium, obtained different compounds if the phosphorus or the soda ammonium was in excess, but in his present research with arsenic he can only obtain the one compound $AsNa_3NH_3$. To prepare this latter substance the sodium and arsenic are both very pure. They are contained in one branch of a double sealed tube, which also contain liquid ammonia gas. A brick-red body is formed, which is slightly soluble in liquid ammonia gas, imparting to it a greenish yellow colour. On evaporating the ammonia very minute crystals are deposited.

Researches on Iodated Borates. — H. Allaire.—Chloroborate of magnesium, which constitutes natural boracite, can be considered as the starting point of a series of compounds of the same crystalline form, in which the chlorine can be replaced by iodine, and the magnesium by zinc, cadmium, manganese, nickel, cobalt, or iron. These compounds are prepared by acting with the vapour of the iodide of the metal on the corresponding borate, at a high temperature and in a current of carbon dioxide; on cooling, crystals of the boracite separate out. The author has prepared the following salts:— $6MgO.8B_2O_3MgI_2$, $6ZnO.8B_2O_3.ZnI_2$, $6CdO.8B_2O_3CdI_2$, $6MnO.8B_2O_3MnI_2$, $6NiO.8B_2O_3.NiI_2$, $6CoO.8B_2O_3.CoI_2$, $6FeO\ 8B_2O_3.FeI_2$.

Solubility of Camphor.—C. Israti and A. Zaharia.—The authors have observed, in the course of synthetic experiments with camphor, that the latter is soluble in water and in hydrochloric acid, which probably transforms it into its derivative—



by direct addition. If to the solution of camphor in concentrated hydrochloric acid a little water is added, a slight precipitate is produced, which dissolves in excess of the same liquid. This is probably due to separation of the body into camphor and hydrochloric acid, the camphor dissolving in excess of water. It is, however, stated by some that camphor is almost insoluble in water. The density of an aqueous solution of camphor at 15° has been found equal to 1·00071. This solubility has been confirmed by the polarimeter; an aqueous solution of camphor saturated in the cold, contained in a tube 22 c.m. long, gave $(\alpha)_D = 0·4°$. As regards the combination of camphor with hydrochloric acid, the body is decomposed by the least trace of water, but the melting-point (about 243°) is much lower than that of camphor. It was also observed that camphor was the most soluble in this acid in the cold.

Researches on Incandescent Electric Lamps charged with a Mixture of Marsh Gas and Air.—H. Couriot and J. Meunier.—A description is given of a method of introducing a mixture of marsh gas and air, in the most explosive proportions, into electric lamps during incandescence. It was found that the incandescence of the filament was at once obscured except at one point, where, in a minute or so, rupture occurred with a faint spark. In no case was there an explosion of the mixture of air and methane; but combustion had occurred, as was shown by the production of water and carbon dioxide, and the disappearance of inflammable gas inside the lamp. Hence the spark, which passed at the moment the filament was ruptured, remained without effect. It has previously been pointed out that incandescent metallic threads are powerless to cause the explosiou of the most explosive mixtures; the same is the case with the lamp filaments.

No. 17, October 24, 1898.

Properties of Calcium.—Henri Moissan.—The author further examines the calcium, the preparation of which was announced in a previous paper. He determines the fusing-point of the metal, by heating it carefully and gradually in a vacuum, to be about 760°. On solidifying the liquid formed, a non-crystalline and soft form of calcium results. The density of the crystalline form is 1·85, whilst non-crystalline calcium sinks in propyl iodide of density 1·78, and floats in allyl iodide of density 1·87.

The non-crystalline form scratches lead, but not chalk. Calcium crystallises in hexagonal plates or derived rhombohedra. With hydrogen the metal forms a crystalline hydride, CaH_2. Calcium is not attacked by chlorine in the cold, but at 400° the chloride is formed. It burns in oxygen at 300° with a brilliant light, and at a dull red heat, in a current of air, both the elements of the atmosphere are fixed. Water attacks calcium at ordinary temperatures, slaked lime being formed.

The Atomic Weight of Tellurium in relation to the Multiple Proportions of the Atomic Weights of other Simple Bodies.—H. Wilde.

Positions of Tellurium and Iodine in the Periodic System of the Elements.—H. Wilde.—These two papers are unsuitable for abstraction.

Calcium Amalgam.—T. Ferée.—The amalgam is very difficult to prepare and almost impossible to keep, owing to its rapid oxidation. The author has prepared small quantities of it by the electrolysis of the chloride, using a mercurial electrode or a porous diaphragm, separating the two electrodes, to prevent the action of the chlorine on the amalgam produced. To avoid rise of temperature in the vessel, cold water is kept circulating round it. The solid amalgam produced by this method is porous and whitish green in colour. It oxidises rapidly in the air and decomposes water. It appears to correspond to the formula Ca_3Hg_4. Heated in a current of hydrogen to a high temperature, it loses more mercury. When heated in a current of nitrogen the nitride is produced.

Action of Metallic Sulphates on Paratungstate of Potassium.—L. A. Hallopeau.—The author studies the double tungstates formed when solutions of metallic tungstates act on potassium paratungstate. He has obtained, by a careful preparation, (1) the paratungstate of potassium and magnesium,—

$$12W.O_3.5(\tfrac{2}{3}K_2O + \tfrac{1}{3}MgO) + 24H_2O,$$

a crystalline body, which acts energetically on polarised light. It loses 17 molecules of water at 100°. (2) the paratungstate of potassium and manganese,—

$$12WO_3.3K_2O.2MnO + 16H_2O,$$

a yellowish-white solid, quite insoluble in water, also acting on polarised light.

Decomposition of a Normal Saturated Hydrocarbon by means of Aluminium Chloride.—C. Friedel and A. Gorgen.—One of the authors, in collaboration with J. M. Crafts, has notified, almost from the beginning of their researches on the syntheses effected by means of aluminium chloride, the decomposing action exercised by this reagent on certain hydrocarbons—*e.g.*, the decomposition (1) of hexamethyl-benzene into durene and other hydrocarbons; (2) of naphthalene into benzene, dinaphthyl, and hydrides of naphthalene; (3) of benzene (at a high temperature) into diphenyl, toluene, and other hydrocarbons. The present paper discusses the treatment of normal hexane with aluminium chloride. The hexane employed was prepared by decomposing propyl iodide with sodium, and also by treating mannite with hydriodic acid, and subsequently submitting the iodide thus obtained to the action of zinc dust. It was introduced in successive stages into the tube containing the aluminium chloride, first passing through a little tube containing bromine, to remove any trace of hexene. The mixture was warmed, and the products passed through a condenser into two U-tubes surrounded with ice, the first containing a little water to retain the hydrochloric acid evolved; the apparatus terminated in a vessel of mercury to collect gaseous products. Finally, a mobile liquid was obtained from the U-tubes, and fractionally distilled. It consisted of unchanged hexane, of pentane, and other more volatile hydrocarbons. The gas collected over mercury consisted chiefly of butane. Thus the action of $AlCl_3$ on hexane consists essentially in removing a CH_3 group, which is replaced by a hydrogen atom and yields pentane. The latter, in its turn, may be similarly converted into butane, which, on account of its volatility, would be but little transformed into propane. At the same time hydrocarbons, richer in carbon than hexane, are found by extracting the aluminium chloride with water.

Amines and Amides derived from Aldehyds.—Marcel Delépine.—In a series of previous papers the author has discussed, from a thermochemical point of view, a certain number of combinations engendered by the action of aldehydes on ammonia or certain amines. The general type of reaction is as follows:—

$$n \text{ aldehyd} + m\left\{\begin{matrix}\text{ammonia}\\ \text{or amine}\end{matrix}\right\} = \text{new body} + pH_2O.$$

The author now classifies the data obtained, with a view to generalising, as far as is possible, from the substances studied.

Journal de Pharmacie et de Chimie, vol. vii., No. 12.

The Value of Tincture of Guiacum as a Test for Oxidising Agents.—Pierre Breteau.—Guiacum resin, which becomes blue on contact with certain oxidising agents, is specially recommended as a sensitive test for blood, sulphate of copper, hydrocyanic acid, phosphorus, &c., either by direct action or through the medium of essence of turpentine. The author has found that this blue colour will appear under circumstances not yet published, and hence errors may easily be made; the phenomenon of turning blue depends on conditions little understood, so that, by even slightly varying these conditions, the reagent can no longer be trusted,—for instance, according to Schœnbein, if equal volumes of tincture of guiacum and aerated turpentine mixed, are shaken up with water, the white precipitate takes an intense blue colour; but according to the author, if this is only slightly modified, and the aerated turpentine is added to a mixture of water and tincture of guiacum, the blue colour does not appear at all, even after prolonged agitation and increase of temperature. Another experiment of Schœnbein's was repeated with blood, using also pure distilled water and absolute alcohol, but no phenomenon occurred; but on the addition of a single drop of essence of turpentine the deep blue colour appeared immediately. It is also shown that traces of copper, which may possibly be present in distilled water, will cause the blue colour to appear without the intervention of essence of turpentine. And again, ordinary ether, alcohol, and benzene have sometimes been found to turn tincture of guiacum blue in the presence of essence of turpentine, while on other occasions, under apparently the same conditions, no colouration has been noticed,—doubtless the presence of copper or other impurities has been the cause of the colouration. Other experiments are described, using paper saturated with tincture of guiacum for the detection of phosphorus and hydrocyanic acid, in which it is shown that the apparent results may be quite misleading, if even only a trace of copper is present.

A Method of Estimating Nitrites in Waters.—Lucien Robin.—Already inserted in full.

Vol. viii., No. 1.

This number contains no matter of chemical interest.

No. 2.

The Hydrolysis of the Pectine of Gentian.—E. Bourquelot and H. Hérissey.—The experiments to which the authors have submitted the pectine of gentian have led to the production of mucic acid by the action of nitric acid, and the production of arabinose, by hydrolysis with the aid of dilute sulphuric acid. The treatment by nitric acid was applied to the pectine obtained by aqueous digestion at 110°, using 12 c.c. of nitric acid to 1 grm. of dried pectine: after heating on the water-bath until the volume is reduced to one-third, it is left to stand for twelve hours, to allow the crystals which form towards

the end of the operation to collect: these are thrown on a double filter and washed with water, and dried first at 30°, then at 100°. The mucic acid formed melts at 215°. The hydrolysis of the pectine by dilute sulphuric acid is effected by keeping 10 grms. of pectine, 500 grms. of water, and 15 grms. of sulphuric acid at 110° for an hour and a half. It is allowed to cool, and filtered; it is then boiled for an hour in a flask fitted with a vertical condenser, neutralised while hot with precipitated chalk, filtered, and evaporated at 60° down to a syrupy consistency. It is then precipitated with alcohol, and the alcoholic liquid evaporated down to the condition of an extract, but no trace of any crystals appeared even after twelve days; ether was therefore added to the alcoholic solution, and from the ethereal solution crystals of arabinose were obtained after partial evaporation.

A General Method for the Preparation of the Mixed Carbonic Ethers of the Fatty and Aromatic Series.—P. Cazeneuve and A. Morel.—Will be inserted in full.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimation of Zinc and Lead.—Will any of your readers kindly give me any information on the estimation of (1) zinc from 2 to 7 per cent, and (2) lead from ½ to 5 per cent, in slags and mattes containing large quantities of iron and lime? The methods should be rapid and fairly accurate.—Cox.

MEETINGS FOR THE WEEK.

Wednesday, 11th.—Society of Arts, 7. (Juvenile Lecture). "Some Ways in which Animals Breathe," by Prof. F. Jeffrey Bell.

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This issue of the Chemical News contains a Supplement devoted to—

A TABULAR ATLAS

OF THE

CHEMISTRY OF THE METALS,

Cs, Rb, and K.

which, it is hoped, will impart a tolerably satisfactory idea of the plan of the work, and the opinions of Eminent Scientists and the Chemical Press concerning it.

In the small fragment given as a specimen of its pages (one-half of one page, and that made up of selections from others), examples of *many divisions* of the "Atlas," and numerous footnotes containing *references to original sources*, are necessarily omitted on account of *deficient space*.

Tabulated Quantitative Analysis, occupying 18 or 20 pages in columnar form, with catch-line headings, could not, therefore, be exhibited.

In that great division, hundreds of methods receive extended consideration; it is arranged in three sub-sections:—

1. Determination of the Element.—Here we find methods (in the case of K) for estimating the metal as $KClO_3$, KCl, K_2PtCl_6, K_2CO_3, K_2SiF_6, KNO_3, K_2SO_4, Bismuth-thiosulphate, KHT, indirectly, spectroscopically, and volumetrically, &c.

2. Analysis of Natural or Technical Products.—Schemes for analysing KBr, $KClO_3$, KCl, KCN, Ferro-, Ferri-, and Sulpho-cyanides, KHO, the Carbonates, and Tartrates; commercial Sulphates, Muriates, &c.; Fertilisers, Plant Ashes, &c.; for the breaking-up of Silicates (two dozen methods); and for the Toxicological Detection of Poisons.

3. Separation from Other Elements.—In all cases the arrangement is as follows:—(*a*). Name of form of combination in which the metal is isolated. (*b*). Variations of the method. (*c*). Brief abstract of plan of procedure. (*d*). Detailed instructions. (*e*). Name of author of method and the reference. (*f*). Comments of chemists on the method, and original experiments.

Toxicology, Metallurgy, and Manufacture also find no place in the specimen; they extend over many pages, presenting features the reader will in vain seek for elsewhere.

On application to the author, a two-page selection of excerpts from the work, containing the explanatory introduction, and accompanied by descriptive circulars, will be forwarded free.

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UNIVERSITY OF ST. ANDREWS.

The University Court of St. Andrews will, at a meeting to be held on January 24. 1899, appoint, for a period of two years as from January 1, 1899, an ADDITIONAL EXAMINER for Graduation in the subject of Chemistry.

Further information may be obtained from Mr. C. S. Grace, W.S., Secretary of the University Court, with whom applications, with testimonials, may be lodged until 14th prox.

St. Andrews, December, 1898.

THE CHEMICAL NEWS.

Vol. LXXIX., No. 2042.

NOTE ON THE DENSITIES OF "ATMOSPHERIC NITROGEN," PURE NITROGEN, AND ARGON.*

By WILLIAM RAMSAY, F.R.S.

M. A. Leduc, in a recent paper ("Recherches sur les Gaz," *Ann. Chim. Phys.*, September, 1898), has discussed the relation between the density of argon, its proportion in atmospheric nitrogen, the density of the latter, and that of pure nitrogen. It appears to me that he has misunderstood some of the data given by Lord Rayleigh, Dr. Kellas, and myself; and as the question whether the found density of argon corresponds with that calculable from the other data, is in itself an interesting one, I have the honour to present this note to the Society.

The data may be divided into two groups, those of Leduc and Schloesing; and those of Rayleigh, Ramsay, and Kellas.

From the first group it is possible to calculate the density of argon, *i.e.*, the crude mixture left after separating oxygen and nitrogen from air.

From the second group the density of argon may be calculated; or if that be assumed, both groups give data for the calculation of that of "atmospheric" nitrogen. It has been thought better to express the results in the form of the weight of one litre of the gas in question; but if it is desired to state them with reference to the density of oxygen = 16, the conversion may be made by means of the weight of a litre of oxygen according to both Lord Rayleigh and M. Leduc.

The data are as follows:—

Weight of 1 litre of	Leduc.	Rayleigh.	Schloesing.	Kellas.	Ramsay.
Air	1·29316	1·29327			
Oxygen	1·42920	1·42952			
Nitrogen ..	1·25070	1·25092			
„ (atmo.)	1·25700	1·25718			
Argon	—	1·78151	—	—	1·7816
„ in "atmo." nitrogen..	—	—	0·01183	0·01186	

Weight of 1 litre argon calculated from Leduc's and Schloesing's figures:—

$0{\cdot}01183x = 1{\cdot}25700 - (1{\cdot}25070 \times 0{\cdot}98817)$; hence $x = 1{\cdot}7828$.

The difference from the value found is 7 in 10,000.

Weight of 1 litre argon calculated from Rayleigh's and Kellas's figures:—

$0{\cdot}01186x = 1{\cdot}25718 - (1{\cdot}25092 \times 0{\cdot}98814)$; hence $x = 1{\cdot}7791$.

The difference from the value found is 13 in 10,000.

Both of these results are quite satisfactory, considering that the nature of the calculation involves a ratio of small differences. The argeement is more striking if the density of "atmospheric" nitrogen is calculated from the figures; for this calculation the weight of 1 litre of argon is assumed to be 1·7815 grms.

Weight of 1 litre of "atmospheric" nitrogen from Leduc's and Schloesing's figures:—

$x = (1{\cdot}7815 \times 0{\cdot}01183) + (1{\cdot}25070 \times 0{\cdot}98817)$; whence $x = 1{\cdot}25698$.

Here the difference is only 2 in 125,000.

From Lord Rayleigh's and Dr. Kellas's figures, we have:—

$x = (1{\cdot}7815 \times 0{\cdot}01186) + (1{\cdot}25092 \times 0{\cdot}98814)$; whence $x = 1{\cdot}25721$.

The difference here is only 3 in 125,000.

It is thus evident that either set of figures gives results as concordant as could be wished; and that the density of "atmospheric" nitrogen is correctly given as the mean of the densities of the constituents, taken in the proportion in which they occur.

* A Paper read before the Royal Society, December 15, 1898.

THE SPECTRUM OF A RADIO-ACTIVE SUBSTANCE.

By EUG. DEMARCAY.

M. and Mdme. Curie have asked me to examine, spectroscopically, a substance consisting chiefly of barium chloride, but supposed by them to contain also a new element. The material was dissolved in distilled water, slightly acidulated with hydrochloric acid. The spark spectrum of this solution was very brilliant. I photographed the spectrum, having prepared two plates, and giving one double the time of exposure of the other. These two plates gave practically identical results. I measured the lines, and was able to see:—(1) Barium, with great intensity of both the strong and weak lines; (2) lead, recognised by its principal lines, which were much more feeble than the others; (3) platinum, due to the electrodes and traces of calcium probably from the solvent; (4) a line, stronger than the weak lines of barium, with wave length 3814·8 (Rowland's scale). This line does not appear to have been attributed to any known element, and is probably due to a new substance, for two reasons. Firstly, that on the plate were no lines, other than these enumerated, except a few feeble air lines, thus excluding the presence of all elements having only weak lines in the neighbourhood of 3814. Secondly, the methods employed for the purification of the substance prevent the possibility of the presence of iron, chromium, cobalt, or nickel, &c. Barium and lead, I am fully assured, give no line coinciding with this.

This line has been measured by means of the two platinum lines, 3818·9 and 3801·5, which enclose it. It is near to and distinct from a bismuth line of moderate intensity.

Conclusion.—The presence of the line 3814·8 confirms the existence of a small quantity of a new element in M. and Mdme. Curie's barium chloride.—*Comptes Rendus*, cxxvii., No. 26.

A COLORIMETRIC METHOD FOR THE ESTIMATION OF SILICA IN WATER.

By A. JOLLES and F. NEURATH.

As is well known, the silica contained in water in the form of hydrated silicic acid, or of an alkaline silicate, is estimated by being transformed into insoluble silica. Although, as a rule, we take no account of the presence of silica in potable water, or in water used for boilers, a simple and rapid method for estimating silica in water might be of service, if only for determining to what point different sorts of glass are attacked by water.

This method enables us to rapidly estimate small quantities of silica, and may be effected on very small quantities of liquid. We know that the alkaline molybdates give with silica in the presence of free nitric acid complex yellow compounds, similar to those which they form with phosphoric and arsenic acids. Among the alkaline silico-molybdates, the silico-molybdate of potassium is the most soluble, and in aqueous solution has a pronounced yellow colour, the intensity of which increases with the temperature, attaining its maximum towards 70° or 80°. This coloured reaction can be utilised for the approximate estimation of silica in water.

For this purpose we use a solution of molybdate of potassium, prepared by dissolving 8 grms. of this salt in 50 cubic c.m. of water, and adding 50 cubic c.m. of pure nitric acid of 1·2 density. We pour 20 cubic c.m. of the water to be examined into a narrow test-tube—the water should stand about 18 c.m. high; we add 1 cubic c.m. of the molybdic solution, and notice the colour obtained. As a colorimetric scale we use a series of test-tubes as near as possible of the same form and dimensions as the first, each containing 20 cubic c.m. of pure distilled water, to which has been added a known quantity of silicate of soda and 1 cubic c.m. of the molybdic solution. All these test-tubes are heated together to 80°. We then compare the colour produced by the water under examination with the colorimetric scale, and thus determine approximately the proportion of silica in the water.

The possible presence of phosphoric or arsenic acid in the water might have some influence on the colouration obtained, and consequently on the result of the analysis. But, generally speaking, the quantity of phosphoric acid present in a natural water is so slight that it can only be detected after concentrating the liquid. As to arsenic acid it is practically never found in natural waters.

However, we might evaporate the sample down with nitric acid several times, separate the silica by filtration, add water to the filtrate, so as to make it up to its original volume, and repeat the colorimetric test on 20 cubic c.m. of this solution. If no yellow colouration is obtained, the absence of both phosphoric and arsenic acids may be considered proved. In the contrary case it must be taken account of in the final calculation.

To verify the exactness of this method we estimated the silica in a number of samples, both by the colorimetric method and by the usual gravimetric method. The results obtained were satisfactory.—*Zeit. für. Augewandte Chemie*, 1898, p. 315.

ON THE

ANALYSIS OF MOLYBDENUM COMPOUNDS.

By HARRY BREARLEY.

(Concluded from p. 5).

The Estimation of Phosphorus.

For various reasons it has become common, after having separated phosphorus as ammonium phospho-molybdate, to proceed to estimate some other constituent of the precipitate, — the volumetric estimation of the reduced molybdenum with permanganate, for instance. It appears as though the molybdenum might easily be estimated gravimetrically by the above process. The operation is certainly not hampered by any such uncertainty as to whether Mo_2O_3, Mo_8O_{13}, or $Mo_{12}O_{19}$, is the state to which the molybdenum is reduced. A further examination will show what the relative advantages of the gravimetric process are.

PS.—The interferences of a very important element—tungsten—is conspicuously absent. It has not been overlooked.

Appendix.

The Estimation of Lead as Molybdate.

In the paper by Chatard (Chemical News, xxiv., 175), previously referred to, he says "I tried to determine lead as molybdate, but without success, as the presence of an excess of the precipitant seems to exert an injurious effect, the filtrate or washings speedily becoming cloudy."

The fact that molybdate of lead is exceptionally insoluble in the solutions from which it may be precipitated, that the ratio Pb : $PbMoO_4$ is lower than the corresponding ratio for either the sulphate or chromate of lead, and that the precipitate may be safely ignited along with the paper, are good reasons for seeking to obviate the difficulty Chatard alludes to.

We have already remarked that, in presence of an excess of lead acetate, the most easily filtrable form of the precipitated lead molybdate is obtained by decomposing the hydrochloric acid, which is keeping the $PbMoO_4$ dissolved, by means of ammonium acetate. If a like procedure be followed in presence of an excess of sodium (or ammonium) molybdate, the lead comes down as a lustrous silky precipitate, somewhat resembling the well-known precipitation of manganese as ammonium manganese phosphate. This precipitate can be filtered and washed with the greatest ease.

The following differences may also be noticed. If an excess of molybdate be added to a solution of lead acidified with HCl only so far as to prevent a precipitate being formed in the cold, then, on warming, the precipitate forms. With an excess of lead acetate the reverse is the case.

The colour of the lead molybdate is more creamy than when precipitated with an excess of lead acetate.

In a series of test analyses the lead acetate used was a commercial sample, and therefore not quite trustworthy as to purity. In order to be assured that the precipitate finally obtained was really pure $PbMoO_4$ it was redissolved in HCl and re-precipitated with an excess of lead acetate. In every case the second result was higher than the first, and pointed to an error which was afterwards found to be inseparable from the use of "acid precipitation" with an excess of molybdate, viz., the contamination of lead molybdate with molybdic acid. The extent of this error may be sufficiently shown by two examples in which an excess of 20 to 30 per cent of precipitant was used.

Grms. lead added.	Lead found.	Error.
0·2284	0·2308	0·0024
0·0914	0·0925	0·0011

This error decreases with the excess of molybdate used, so that, if the precipitate be re-dissolved in hydrochloric acid and re-precipitated with ammonium acetate without any further addition of either $(NH_4)_2$, MoO_4, or $Pb\bar{A}_2$, the ideal conditions are almost attained and the results are very accurate.

An equally accurate result is obtainable by re-precipitating with an excess of lead acetate, and calculating the difference between the first and second weights of $PbMoO_4$ into MoO_3, and subtracting the number found from the first weight. Thus an actual example gave—

Weight of first precipitate of $PbMoO_4$	0·4093 grm.
,, second ,, ,,	0·4210 ,,
	,,
	0·0177 ,,

0·0117 $PbMoO_4$ = 0·0046 MoO_3.

0·4093 − 0·0046 = 0·4047 grm. of lead molydate, instead of 0·4051 grm. which it should weigh theoretically.

The acid precipitation is set forth at such length because here, as in the converse case, it is especially valuable where lead is being estimated, without previous separation, in a great number of its combinations and alloys with other metals.

Chatard's form of precipitation was now repeated, in order to see if a compact pulp filter could overcome the difficulty he mentions. The filtered and unfiltered portions were hardly distinguishable from each other, and, like those unfiltrable clayey waters, prolonged standing showed no appreciable settling. But this difficulty is due altogether to the fact that the experiment was made, both in Chatard's case and my own, with practically pure materials. On adding ammonium chloride to the unfiltrable solution the precipitate agglomerates, and on digesting becomes granular and easily filtrable. For pure solutions, then, and probably in the presence of such elements as have been shown not to interfere with the converse opera-

tion carried out in the ordinary way, it is simply necessary to add ammonium chloride either before or along with the excess of the alkaline molybdate. The lead separates as pure $PbMoO_4$, and re-precipitation is unnecessary.

Test Analyses.

Lead added.	Lead found.	Error.
0.3198	0·3200	0·0002
0·2284	0·2285	0·0001
0·1371	0·1370	0·0001
0·0914	0·0914	0·0000
0·0457	0·0457	0·0000
0·0229	0·0231	0·0002

Totley, near Sheffield.

DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.*

By J. MERRITT MATTHEWS.

(Continued from p. 7).

4. Action of Fatty and Aromatic Amines.

It was in this field that positive results were at last encountered. Silicon, titanium, and tin tetrachlorides all give compounds with the amines, and analogy would lead us to expect that the chlorides here used would behave in a similar manner, as indeed was the case. These derivatives with the amine bases, including ammonia, are apparently peculiar additive products, showing that these tetrachlorides, in common with the other chlorides of this group, possess an acid character.

The compounds herein described were obtained by the simple addition of the pure anhydrous reagents to the solutions of the respective tetrachlorides. The zirconium and thorium derivatives, for the most part, were white flocculent precipitates; the lead salts, however, gave compounds of various colours.

The analysis of these derivatives was carried out in the following manner:—With the zirconium and thorium compound a weighed quantity was placed in a small beaker-glass and covered with nitric acid containing a solution of silver nitrate, and gently warmed. This sufficed to decompose the substance, the chlorine present being precipitated as silver chloride. The liquid was diluted with water, the chloride filtered off, and from its weight the chlorine was estimated. Excess of ammonia water was added to the filtrate, and the resulting precipitate of zirconium or thorium hydroxide was filtered off and ignited to the corresponding dioxide, from the weight of which the zirconium or thorium was estimated. The nitrogen present in the ammonia derivatives was determined by heating a portion with a strong solution of sodium hydroxide, and passing the evolved ammonia into a standardised solution of hydrochloric acid, and either titrating the excess of acid with standard alkali, or precipitating the ammonia in the usual manner with a solution of platinic chloride, and from the weight of the platinum left after ignition calculating the quantity of nitrogen. With the amine derivatives the Kjeldahl method was employed; and the Will and Varrentrap method was used for the quinoline and pyridine compounds. The lead compounds were decomposed with warm nitric acid, and the lead determined as sulphate by evaporation with sulphuric acid in the usual manner, the chlorine being determined by heating the compound with sulphuric acid in a distilling flask, passing the evolved hydrochloric acid gas into a solution of silver nitrate, and weighing the silver chloride as usual. The nitrogen present was estimated as with the zirconium and thorium derivatives.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx., No. 11. From author's thesis for the Degree of Doctor of Philosophy.

A. *Ammonia.*

Paykull (*Ber. d. Chem. Ges.*, vi., 1467) obtained a compound of zirconium tetrachloride with ammonia by heating the former with NH_4Cl, and to this compound he ascribes the formula $ZrCl_4{\cdot}4NH_3$. Besson (*Compt. Rend.*, cx., 240) has also obtained an ammonia derivative with silicon tetrachloride, giving it the formula $SiCl_4{\cdot}6NH_3$. With tin tetrachloride Rose (*Pogg. Ann.*, xx., 147) obtained the compound $SnCl_4{\cdot}4NH_3$, though Persoz (*Ann. Chim. Phys.*, xlvi., 305) claims to have made $SnCl_4{\cdot}6NH_3$. With titanium tetrachloride Rose (*Pogg. Ann.*, xx., 147) obtained the compound $TiCl_4{\cdot}4NH_3$, though Persoz (*vide supra*) gives the formula as $TiCl_4{\cdot}6NH_3$.

a. Zirconium Tetrachloride, $ZrCl_4{\cdot}8NH_3$.—On passing dry ammonia gas into the solution of zirconium tetrachloride, a white flocculent precipitate was immediately produced, with considerable evolution of heat. This compound on drying appeared to be stable in the air, though on gently heating it gave off fumes of ammonium chloride. Its analysis showed the presence of eight molecules of ammonia.

I. 0·5625 grm. material gave:—

0·8729 grm. silver chloride = 0·2161 grm. chlorine = 38·42 per cent chlorine.

0·1860 grm. zirconium dioxide = 0·1374 grm. zirconium = 24·44 per cent zirconium.

II. 0·1862 grm. material gave:—

0·2881 grm. silver chloride = 0·0713 grm. chlorine = 38·30 per cent chlorine.

0·0623 grm. zirconium dioxide = 0·0460 grm. zirconium = 24·71 per cent zirconium.

0·0624 grm. material gave 0·0228 grm. ammonia = 36·60 per cent ammonia.

0·5625 grm. material gave 0·2084 grm. ammonia = 37·05 per cent ammonia.

	Calculated for $ZrCl_4{\cdot}8NH_3$.	Found. I.	Found. II.
Chlorine	38·52	38·42	38·30
Zirconium	23·58	24·44	24·71
Ammonia	36·90	36·60	37·05

$ZrCl_4{\cdot}2NH_3$.—On passing dry ammonia gas over the solid zirconium tetrachloride contained in a porcelain boat, a considerable evolution of heat was observed, evidently showing that combination resulted. The compound thus obtained was white in colour, fumed in the air, and rapidly took up moisture, rendering it difficult to analyse with accuracy.

0·5304 grm. zirconium tetrachloride, after being treated with ammonia gas for two hours, on re-weighing gave 0·6247 grm.

This on analysis gave:—

1·3778 grm. silver chloride = 0·3163 grm. chlorine = 50·67 per cent chlorine.

0·2927 grm. zirconium dioxide = 0·2163 grm. zirconium = 34·62 per cent zirconium.

	Calculated for $ZrCl_4{\cdot}2NH_3$.	Found.
Chlorine	51·81	50·67
Zirconium	33·21	34·26
	Grm.	Grm.
Increase in weight	0·0917	0·0943

$ZrCl_4{\cdot}4NH_3$.—On heating zirconium tetrachloride in a current of dry ammonia gas, a compound was obtained which was white in colour, and unstable on exposure to the air.

0·4713 grm. zirconium tetrachloride being gently heated (to about 100° C.) in ammonia gas, on re-weighing gave 0·6123 grm.

This on analysis gave:—

1·1397 grm. silver chloride = 0·2821 grm. chlorine = 46·07 per cent chlorine.

0·2588 grm. zirconium dioxide = 0·1912 grm. zirconium = 31·23 per cent zirconium.

	Calculated for $ZrCl_4 \cdot 4NH_3$.	Found.
Chlorine	47·24	46·07
Zirconium	30·14	31·23
	Grm.	Grm.
Increase in weight	0·1378	0·1410

These results seem to indicate that zirconium tetrachloride may be combined with ammonia in three proportions, depending upon the conditions under which the combination is brought about. When in ethereal solution it takes up eight molecules of ammonia, giving $ZrCl_4 \cdot 8NH_3$; the dry salt unaided by heat gives $ZrCl_4 \cdot 2NH_3$; and with the aid of heat the latter also gives the compound $ZrCl_4 \cdot 4NH_3$. All of these bodies are white in colour, the first one only being stable in the air. The last of the above derivatives seems to be identical with the one obtained by Paykull.

b. Thorium Tetrachloride.—As the field of thorium derivatives has not been investigated in any very exhaustive manner, one would not be likely to encounter any preceding research in the rather remote class of compounds herein dealt with. Chydenius (*Ysb. Chem.*, 1863, 194), however, has prepared a derivative of thorium tetrachloride with ammonium chloride, to which he has given the formula $ThCl_4 \cdot 8NH_4Cl$. It is of interest to note that the compound prepared in this present research also contains the same molecular proportions of ammonia to thorium.

$ThCl_4 \cdot 8NH_3$.—Dry ammonia gas passed into the solution of thorium tetrachloride produced a white flocculent precipitate, which, on drying, continued stable in the air. On heating it decomposed with the evolution of fumes of ammonium chloride.

I. 0·5870 grm. material gave :—

0·6526 grm. silver chloride = 0·1616 grm. chlorine = 27·52 per cent chlorine.

0·3054 grm. thorium dioxide = 0·2684 grm. thorium = 45·73 per cent thorium.

II. 0·6212 grm. material gave :—

0·5928 grm. silver chloride = 0·1715 grm. chlorine = 27 61 per cent chlorine.

0·3212 grm. thorium dioxide = 0·2824 grm. thorium = 45·46 per cent thorium.

0·5172 grm. material gave 0·1366 grm. ammonia = 26·41 per cent ammonia.

	Calculated for $ThCl_4 \cdot 8NH_3$.	Found. I.	Found. II.
Chlorine	27·80	27·52	27·61
Thorium	45·55	45·73	45·46
Ammonia	26·64	26·41	—

$ThCl_4 \cdot 6NH_3$.—On allowing dry ammonia gas to pass over a portion of thorium tetrachloride placed in a porcelain boat, a considerable evolution of heat was observed, the ammonia evidently reacting with the salt. The resulting compound was white in colour, and fumed in moist air, though it appeared to be more stable than the corresponding zirconium derivative obtained under the same conditions.

0·4217 grm. material, on being treated with ammonia gas for two hours, on re-weighing gave 0·5352 grm. This on analysis gave :—

0·6274 grm. silver chloride = 0·1553 grm. chlorine = 29·01 per cent chlorine.

0·3021 grm. thorium dioxide = 0·2656 grm. thorium = 49·62 per cent thorium.

	Calculated for $ThCl_4 \cdot 6NH_3$.	Found.
Chlorine	29·79	29·01
Thorium	48·80	49·62
	Grm.	Grm.
Increase in weight	0·1148	0·1135

On gently heating thorium tetrachloride to about 100° C. in a current of ammonia gas, a compound was obtained identical with the one just described above; it possessed the same appearance, and analysed for the same formula. At a higher temperature decomposition seemed to take place, and copious fumes of ammonium chloride were formed.

c. Lead Tetrachloride, $PbCl_4 \cdot 4NH_3$.—On treating the chloroform solution of lead tetrachloride with dry ammonia gas, an orange-yellow precipitate was at first produced, which rapidly became white in colour as more ammonia was absorbed. A great amount of heat was evolved in the reaction, and the compound continued stable in the air.

I. 0·3600 grm. material gave :—

0·2597 grm. lead sulphate = 0·1774 grm. lead = 49·30 per cent lead.

0·2614 grm. material gave :—

0·3205 grm. silver chloride = 0·0816 grm. chlorine = 33·76 per cent chlorine.

II. 0·2582 grm. material gave :—

0·1874 grm. lead sulphate = 0·1281 grm. lead = 49·62 per cent lead.

0·2075 grm. material gave :—

0·2844 grm. silver chloride = 0·0704 grm. chlorine = 33·92 per cent chlorine.

0·4201 grm. material gave :—

0·3817 grm. platinum = 0·0664 grm. ammonia = 15·81 per cent ammonia.

	Calculated for $PbCl_4 \cdot 4NH_3$.	Found. I.	Found. II.
Lead	49·88	49·30	49·62
Chlorine	34·05	33·76	33·92
Ammonia	16·07	15·81	—

$PbCl_4 \cdot 2NH_3$.—By using a more concentrated solution of lead tetrachloride, and interrupting the treatment with ammonia gas before all of the lead salt was neutralised, an orange-yellow precipitate was obtained. This fumed in the air and decomposed on standing. Its analysis indicated the above formula.

0·3017 grm. material gave :—

0·2375 grm. lead sulphate = 0·1622 grm. lead = 53·75 per cent lead.

0·2332 grm. material gave :—

0·3525 grm. silver chloride = 0·0873 grm. chlorine = 37·42 per cent chlorine.

0·2716 grm. material gave :—

0·1430 grm. platinum = 0·0249 grm. ammonia = 9·16 per cent ammonia.

	Calculated for $PbCl_4 \cdot 2NH_3$.	Found.
Lead	54·16	53·75
Chlorine	37·00	37·42
Ammonia	8·85	9·16

B. *Methylamine.*

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 4CH_3NH_2$.—On conducting the vapours of methylamine into the solution of zirconium tetrachloride, a white flocculent precipitate was formed. Analysis showed that it followed the same general type as the other derivatives.

I. 0·2417 grm. material gave :—

0·3833 grm. silver chloride = 0·0949 grm. chlorine = 39·26 per cent chlorine.

0·0838 grm. zirconium dioxide = 0·0619 grm. zirconium = 25·62 per cent zirconium.

II. 0·5432 grm. material gave :—

0·8674 grm. silver chloride = 0·2147 grm. chlorine = 39·53 per cent chlorine.

0·1786 grm. zirconium dioxide = 0·1339 grm. zirconium = 25·65 per cent zirconium.

0·6021 grm. material gave :—

0·1165 grm. ammonia = 0·0969 grm. nitrogen = 15·95 per cent nitrogen.

	Calculated for $ZrCl_4{\cdot}4CH_3NH_2$.	Found. I.	Found. II.
Chlorine	39·82	39·36	39·53
Zirconium ..	25·41	25·62	25·65
Nitrogen	16·18	15·95	—

b. Thorium Tetrachloride, $ThCl_4{\cdot}4CH_3NH_2$.—The compound obtained with thorium tetrachloride showed the presence of four molecules of the base. Indeed this seems to be the general type after which all these derivatives are modelled.

0·6513 grm. material gave:—
0·7451 grm. silver chloride = 0·1802 grm. chlorine = 28·32 per cent chlorine.
0·3461 grm. thorium dioxide = 0·3040 grm. thorium = 46·71 per cent thorium.
0·5318 grm. material gave:—
0·0712 grm. ammonia = 0·0587 grm. nitrogen = 11·03 per cent nitrogen.

	Calculated for $ThCl_4{\cdot}4CH_3NH_2$.	Found.
Chlorine	28·48	28·32
Thorium	46·65	46·71
Nitrogen	11·24	11·03

c. Lead Tetrachloride, $PbCl_4{\cdot}4CH_3NH_2$.—The compound obtained with lead tetrachloride was also white in colour, and stable in the air. Analysis proved it to be analogous to the preceding derivatives.

0·2506 grm. material gave:—
0·2969 grm. silver chloride = 0·0735 grm. chlorine = 29·32 per cent chlorine.
0·2716 grm. material gave:—
0·1757 grm. lead sulphate = 0·1200 grm. lead = 44·17 per cent lead.
0·2517 grm. material gave:—
0·2005 grm. platinum = 0·0289 grm. nitrogen = 11·42 per cent nitrogen.

	Calculated for $PbCl_4{\cdot}4CH_3NH_2$.	Found.
Chlorine	30·02	29·32
Lead	43·76	44·17
Nitrogen	11·84	11·42

C. *Ethylamine.*

a. Zirconium Tetrachloride, $ZrCl_4{\cdot}4C_2H_5NH_2$.—As would be expected from its behaviour with the preceding amine, zirconium tetrachloride was found to yield a derivative with ethylamine.

0·5418 grm. material gave:—
0·7478 grm. silver chloride = 0·1856 grm. chlorine = 34·26 per cent chlorine.
0·1619 grm. zirconium dioxide = 0·1196 grm. zirconium = 22·08 per cent zirconium.
0·6516 grm. material gave:—
0·0861 grm. ammonia = 0·0709 grm. nitrogen = 10·89 per cent nitrogen.

	Calculated for $ZrCl_4{\cdot}4C_2H_5NH_2$.	Found.
Chlorine	34·42	34·26
Zirconium	21·96	22·08
Nitrogen	10·79	10·89

b. Thorium Tetrachloride, $ThCl_4{\cdot}4C_2H_5NH_2$.—Ethylamine gave a white compound with thorium tetrachloride.

0·2102 grm. material gave:—
0·2137 grm. silver chloride = 0·0528 grm. chlorine = 25·12 per cent chlorine.
0·0995 grm. thorium dioxide = 0·0874 grm. thorium = 41·58 per cent thorium.
0·5912 grm. material gave:—
0·0712 grm. ammonia = 0·0587 grm. nitrogen = 9·92 per cent nitrogen.

	Calculated for $ThCl_4{\cdot}4C_2H_5NH_2$.	Found.
Chlorine	25·60	25·12
Thorium	41·94	41·58
Nitrogen	10·10	9·92

c. Lead Tetrachloride, $PbCl_4{\cdot}4C_2H_5NH_2$.—Ethylamine gave at first a yellow precipitate with the solution of lead tetrachloride, which went over to a white compound on the addition of more ethylamine.

0·2072 grm. material gave:—
0·2220 grm. silver chloride = 0·0550 grm. chlorine = 25·52 per cent chlorine.
0·2506 grm. material gave:—
0·1459 grm. lead sulphate = 0·0996 grm. lead = 39·76 per cent lead.
0·3817 grm. material gave:—
0·2746 grm. platinum = 0·0394 grm. nitrogen = 10·32 per cent nitrogen.

	Calculated for $PbCl_4{\cdot}4C_2H_5NH_2$.	Found.
Chlorine	26·84	26·52
Lead	39·13	39·76
Nitrogen	10·59	10·32

(To be continued).

CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.*

By A. B. PRESCOTT and H. M. GORDIN.†

The Periodides in Respect to Completeness of Precipitation.

In aqueous solutions of salts of the alkaloids, one of the most delicate of qualitative reagents is iodopotassium iodide. Wormley gives the limit of this precipitation, for the chief medicinal alkaloids, as from $\frac{1}{100000}$ to $\frac{1}{1000000}$ of a grain of the alkaloid in one grain of water; that is, from 0·0000013 to 0·0000007 grm. in 1 c.c. of water ("Microchemistry of Poisons," 1885, Tabular View). The precipitate is not appreciably soluble in excess of the reagent, an advantage over several other qualitative precipitations of alkaloids in general. In some cases the precipitate is appreciably soluble in excess of the alkaloidal salt, and this condition is one most easy to avoid. The potassium iodide solution of iodine was recommended as a reagent for alkaloids by Bouchardat, a medical writer in Paris, in 1839 (Bouchardat, 1839, *Compt. Rend.*, ix., 475; *L'Institut*, vii., 358). This precipitation, however, was proposed as an antidote for strychnine, in cases of poisoning of dogs. Further, see Donné (*Ann. Chim. Phys.* (2), xxxviii., 82).

As a volumetric solution, the decinormal solution of iodine with potassium iodide was first proposed by Wagner, in 1861 (R. Wagner, Dingler's *Poly. J.*, clxi., 40; *Ztschr. Anal. Chem.*, i., 102), and the decinormal strength is generally the most suitable for volumetric use.

Historical as to the Formation of Perhalides in General.

The formation of the alkaloidal periodides was first made a subject of systematic observation by Jörgensen, at Copenhagen, in 1869 (Jörgensen, 1869-1878, *J. Prakt. Chem.* (2), ii., 347, 433; iii., 145, 328; xiv., 213, 356; xv., 65, 418; xvi., 352; *Ber. d. Chem. Ges.*, ii., 460), and the masterly researches of this Danish chemist, extending over nine years, afford a model of logical inquiry into chemical structure. A still wider study of all periodides and some other perhalides of organic bases was commenced in 1887 by Professor Geuther (A. Geuther, *Ann. Chem. Pharm.* (Liebig), ccxl., 66 91, with lists of the

* The portion of this article which concerns atropine was given in substance in the *Journ. Am. Chem. Soc.*, xx., 329, under the title, "Atropine Periodides and Iodomercurates," by H. M. Gordin and A. B. Prescott (reprints). Also that concerning morphine and opium, except the "Results of Opium Assay," appeared in Kremers' *Pharmaceutical Archives*, June, 1898, i., 121, under the title, "A Volumetric Assay of Opium," by H. M. Gordin and A. B. Prescott (reprints).

† In the work of Research Committee D, Section 2, Committee on Revision of the Pharmacopœia of the United States.

organic periodides previously obtained), of Jena, but was cut short by his death in 1889. Among various periodides reported of later years have been picoline periodides by William Ramsay in 1878 (*Phil. Mag.* (5), ii., 269; iv., 241; vi., 19); cæsium and rubidium periodides by Wells, and others in 1893 (*Am. J. Sci.* (3), xliv., 42; xliii., 17); iodonium periodides by Victor Meyer in 1894 (*Ber. d. Chem. Ges.*, xxvii., 1594); sulphon periodides by Kastle in 1894 (*Am. Chem. J.*, xvi., 116); periodides of diazo bodies by Hantsch in 1895 (*Ber. d. Chem. Ges.*, xxviii., 2754); halogen addition-products of the anilides by Wheeler and others in 1896-97 (*Am. Chem. J.*, xviii., 85; xix., 672); perhalides of aliphatic amines by Norris in 1898 (*Am. Chem. J.*, xx., 51); mixed perhalides of alkyl anilines by Samtleben in 1898 (A. Samtleben, *Ber. d. Chem. Ges.*, xxxi., 1141).

In this laboratory since 1895 the perhalides and various double halides of pyridine have been obtained,* also the perhalides of caffeine (Gomberg, Perhalides of Caffeine, *Journ. Amer. Chem. Soc.*, xviii., 347-378), and work on picoline perhalides is in hand. In the course of work upon an entirely different inquiry, a new order of perhalides has just been obtained, a periodide of brom-triphenylmethane.†

It is of interest to inquire what classes of compounds are liable to the formation of perhalides, and this inquiry has a special interest when it is proposed to estimate a single class of compounds, in vegetable drugs or their extracts, by formation of periodide. In general terms the reply is easily given, that periodides are limited to the organic basis, that is the more or less basal compounds of the nitrogen family of elements, and the inorganic alkalies. It is remarkable that the iodonium compounds yield periodides, which is quite in accord with the claim of Victor Meyer that in these bodies iodine itself strangely serves (with the benzene ring) as a base-forming element like a member of the nitrogen family. This view is supported further by Gomberg's production at this time of a periodide of a triphenylmethane derivative, as cited just above.

At present it seems highly improbable that any plant constituent other than the alkaloids, in the larger sense of organic bases, are of the sort of bodies which can form periodides in precipitation. Moreover, Wagner's reagent is used in a qualitative way along with plant analysis to an extent likely to call attention to any interference with its use for alkaloids. From the work of Wheeler it is evident that periodides may be formed by acid amides, but probably not by precipitation in dilute solutions. The formation of iodonium periodides, and a sulphone periodide, indicate that the limits of formation of perhalides cannot yet be declared, and it will be well for analysts to be watchful of new developments.

Historical as to Analytical Use of Periodides.

The volumetric use of a potassium iodide aqueous solution of iodine dates from Wagner in 1861, and the solution in decinormal strength of iodine is named Wagner's reagent.

(Note.—R. Wagner, 1861, *Ding. Poly. J.*, clxi., 40; *Ztschr. Anal. Chem.*, i., 102. Wagner wisely avoided washing the precipitate, but he failed to add the solution of alkaloid to that of iodine:—"Man versetzt die Losung der Basen, deren Menge man bestimmen will, mit überschüssiger Iod lösung, filtrirt und bestimmt in einem gemessenen Theil des Filtrats mit unterschwefligsaurem Natron das überschüssige Iod." As periodides had not then been prepared and analysed, the iodine factors of Wagner were empirical, and, as the higher periodides are not invariably the sole products when iodine solution *is added to* the alkaloid solution, the factors adopted proved unsatisfactory. It is noteworthy that "Mayer's reagent" was so nearly contemporaneous with Wagner's in publication. The potassium mercuric iodide method of volumetric estimation dates from 1862—*Proc. Am. Pharm. Assoc.*, 230; *Am. J. Pharm.*, xxxv., 20; Chemical News, vii., 159; viii., 177, 189. Of special American interest is Dr. F. Hoffmann's biography of Ferdinand F. Meyer as a New York chemist, *Pharm. Rundschau*, 1894, xii., 125, and of more general interest, Professor Schaer's history of Mayer's alkaloid reagent, *Pharm. Rundschau*, xii., 142).

This iodine solution was tried briefly by Schweissinger in 1885 (*Arch. Pharm.*, 1885, 611), and at length by Kippenberger in 1895 (K. Kippenberger, 1895; *Ztschr. Anal. Chem.*, xxxiv., 317; xxxv., 407, 422), but both seem to have obtained the lower periodides, at least in part, in their methods of estimation. The last-named author proceeded upon a volumetric deduction of a general formation of tri-iodides, and sought to so vary the conditions as to support the factor of a tri-iodide. In 1896, Gomberg (*Journ. Amer. Chem. Soc.*, xviii., 331), along with his production of caffeine perhalides above referred to, established the volumetric estimation of caffeine in acidulated solutions as a pentaiodide, and this was used, with a method of extraction from Kola, throughout the work of Mr. Knox and one of us (Knox and Prescott, *Proc. Am. Pharm. Assoc.*, xliv., 128; xlv., 131; *Journ. Amer. Chem. Soc.*, xix., 63; xx., 34) upon the caffeine compound of kola with complete satisfaction.

The Higher Periodides in respect to Constancy of Composition.

The number of the periodides of pyridine is representative of the fact that most of the alkaloids of pyridine-derived constitution will form each more than one periodide, according to conditions. We find it is more expedient to secure the exclusive formation of the higher periodide, by needful conditions, than that of any other periodide obtainable. The higher periodides are not surpassed in completeness of precipitation, and they are sufficiently stable. At least this is true of those alkaloids included in this report. In future reports we desire to be able to give analyses of all the readily obtained periodides of each of the alkaloids reported upon in this article.

If we add the iodopotassium iodide solution to the solution of an alkaloidal salt, keeping from the beginning to the end the alkaloid in excess, it is generally the lowest periodide (in most cases a tri-iodide) that is formed, but if the order be reversed and the alkaloidal solutions added to the iodopotassium iodide solution, keeping all the time a large excess of iodine, it is generally the highest periodide that is formed. We have found this rule to hold good with atropine, strychnine, brucine, aconitine, and several other alkaloids. It was mainly the lower periodides of alkaloids that were made and described by Jörgensen; they are generally very stable, and can be easily obtained in crystalline form by crystallisation from some suitable solvent. As to the higher periodides, some of them are stable enough to be re-crystallisable; many others are easily decomposed in solution into free iodine and lower periodides. Atropine enneaiodide belongs to the first class; strychnine heptaiodide and brucine heptaiodide belong to the second.

Following the above-mentioned rule, we have succeeded in obtaining an enneaiodide of atropine, $C_{17}H_{23}NO_3HI\ I_8$; a heptaiodide of strychnine, $C_{21}H_{22}N_2O_2HI.I_6$; a heptaiodide of brucine, $C_{23}H_{26}N_2O_4HI.I_6$, and, as it is probable, a tri-iodide and a heptaiodide of aconitine. The tetraiodide of morphine, obtained by Jörgensen is the only periodide of morphine that we have been able to make by precipitation.

* Prescott, the Periodides, *Journ. Am. Chem. Soc.*, xvii., 775; *Pharm. Rundschau*, xiii., 233. Prescott and Trowbridge, Periodides of Pyridine, *Journ. Am. Chem. Soc.*, xvii., 859. Flinterman and Prescott, Dipyridine Methylene Dibromide, *Ibid.*, xviii., 28. Prescott, Pyridine Alkyl Iodides, *Ibid.*, xviii., 91. Trowbridge, Periodides of Pyridine, *Ibid.*, xix., 322. Trowbridge and Diehl, Halides and Perhalides of Pyridine, *Ibid.*, xix., 558.

† See paper by Gomberg read at Boston meeting of the American Chemical Society, August, 1898, and to be published in a subsequent number of the *Journ. Am. Chem. Soc.*

These compounds are of the common order of alkaloidal hydriodide periodides. The single atom of iodine in the normal hydriodide is transposed by silver nitrate solution with precipitation, but does not respond to reducing agents. The rest of the iodine, being additive to the first atom of this element, is very easily taken up by reducing agents, such as sulphur dioxide, a thiosulphate, or powdered zinc.

Preparation of the Higher Periodides in Purity for Analysis.

The periodides, of which analysis is given in this paper, were all made according to the following method:—1 grm. of the alkaloid was dissolved in about 200 c.c. of water acidulated with sulphuric or hydrochloric acid, and the solution poured, in small quantities at a time, into 500 c.c. of water containing 1 per cent free iodine and 1½ per cent potassium iodide. After shaking until the liquid became perfectly clear, the mother-liquor was removed in filtration by means of a pump, the precipitate well washed with cold water, and dried first on porous plates and then in a vacuum over sulphuric acid. For the aconitine triiodide the order of mixing was reversed, and an excess of aconitine kept during the whole operation. After drying, the precipitate was re-crystallised from alcohol. These periodides, so prepared, were subjected to analysis by the method given under atropine below, and as stated further under the several alkaloids, and from the results of the analysis the volumetric factor of free iodine for each alkaloid was determined.

Atropine Enneaiodide and its Analysis.

The enneaiodide, obtained as above described, is a very dark brown, almost black powder, quite permanent in dry air, and has only a slight odour of iodine. It is very difficultly soluble in ether, chloroform, benzene, or carbon disulphide, but is soluble in alcohol, very freely when hot. In cold water it is insoluble; hot water decomposes it quickly; it is also decomposed by concentrated solutions of potassium iodide. At 90° C. it commences to give up iodine vapours, and at 140° C. melts to a dark liquid. To obtain it in crystalline form it is first washed with a little cold alcohol to remove traces of free iodine, and then dissolved in warm alcohol. On cooling it crystallises out in dark green prisms and leaflets, having the same properties as the non-crystallised body. In analysis we estimated the additive iodine volumetrically, and the total iodine both gravimetrically and volumetrically.

To estimate the additive iodine a small quantity of the enneaiodide is dissolved in very little alcohol, an excess of a standardised solution of sodium thiosulphate added, and the excess titrated back with a standard solution of iodine, using starch as the indicator.

For total iodine the substance is covered with an excess of powdered metallic zinc and some water, and then boiled gently for ten or fifteen minutes, taking care to prevent loss by spurting; the mixture is then thrown upon a filter, and the containing flask and the filter are thoroughly washed with hot water. The iodine in the zinc iodide thus formed can either be estimated by precipitation with silver nitrate and nitric acid, and weighing as silver iodide, or it is precipitated with an excess of a standardised solution of silver nitrate, and the excess titrated back with a standard solution of ammonium thiocyanate, using ferric nitrate as indicator.

In the following analyses the standard silver nitrate solution was made to correspond with 1 per cent of iodine, and the ammonium thiocyanate solution to correspond, c.c. per c.c., with the silver nitrate solution. The standard solution of iodine contained 1 per cent of iodine, and the sodium thiosulphate solution corresponded, c.c. per c.c., with the iodine solution.

Analysis of the Atropine Enneaiodine not Re-crystallised:—In the volumetric estimation for total iodine, 0·15225 grm. required 12·2 c.c. of the silver nitrate solution. For the iodine removed by reduction, 0·19255 grm. required 13·7 c.c. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_3{\cdot}HI{\cdot}I_8$.	Found.
Iodine by reduction	70·88	71·15
Total iodine	79·74	80·13

In the gravimetric estimation from 0·218 grm. 0·3207 grm. silver iodide was obtained.

	Calculated for $C_{17}H_{23}NO_3HI{\cdot}I_8$.	Found.
Total iodine	97·74	79·48

Analysis of the Atropine Enneaiodide Re-crystallised from Alcohol.—The methods employed were the same as with the non-recrystallised compound, and the standard solutions of the same strength.

In the volumetric estimation of total iodine, 0·12685 grm. required 10·1 c.c. of the silver nitrate solution. For the iodine removed by reducing agents, 0·23105 grm. required 16·4 c.c. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_3{\cdot}HI{\cdot}I_8$.	Found.
Total iodine	79·74	79·62
Iodine by reduction	70·88	70·98

In the gravimetric estimation of total iodine, 0·2031 grm. gave 0·30035 grm. silver iodide.

	Calculated for $C_{17}H_{23}NO_3{\cdot}HI{\cdot}I_8$.	Found.
Total iodine	79·74	79·90

The constitution of the compound is that of atropine hydriodide octaiodide. The alkaloidal hydriodide is formed, in the (acidulated) solution, by transposition of the alkaloidal salt taken with potassium iodide. Thus:—

$$C_{17}H_{23}NO_3{\cdot}HCl + KI + I_8 = C_{17}H_{23}NO_3{\cdot}HI{\cdot}I_8 + KCl.*$$

Therefore the ratio of the free iodine consumed, to the absolute atropine, is the ratio of I_8 to $C_{17}H_{23}NO_3$, equal to ratio 1012·24 to 288·38, or of 1 of iodine to 0·2849 of atropine.† And 1 c.c. of decinormal iodine solution consumed is equivalent to 0·0036048 grm. of the atropine. *This decinormal factor* was found to hold good under the control estimations reported further on.

(To be continued).

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.‡

By THEODORE WILLIAM RICHARDS.

In a recent critical discussion of Stas's work upon the atomic weight of carbon, Dr. Alexander Scott (*Journ. Chem. Soc. Trans.*, 1897, lxxi., 559), of London, had occasion to repeat some observations made at Harvard several years ago (*Proc. Amer. Acad.*, xxvi., 281; *Z. Anorg. Chem.*, i., 196). According to these observations, cupric oxide made from cupric nitrate had been found usually to contain several times its volume of occluded gases, chiefly nitrogen, and moreover it was shown that this gas resulted from the decomposition of minute traces of residual nitrate confined in the inmost recesses of the masses of oxide. Dr. Scott, however, could not find as much as one-tenth of this amount of gas in his material. Since he was unable to explain the apparent discrepancy, it is

* For experimental verification of this equation see a later paragraph in the *Journ. Am. Chem. Soc.*

† The atomic weights taken were those of L. Meyer and K. Seubert, H=1.

‡ Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 22; also *American Chemical Journal*, November, 1898.

one of the objects of the present paper to shed a clearer light upon the subject.

The essential point which escaped Dr. Scott's notice is this:—The temperature of ignition is the most important condition determining the amount of the occluded gases. When the temperature is very high, nearly all of the imprisoned impurity is set free. To quote Dr. Scott's words, his oxide was exposed "for varying times to a full red heat in a muffle heated with gas." It is well known that at a temperature of about 1000° cupric oxide melts, with a very considerable loss of oxygen. It is obvious, then, that temperatures in this neighbourhood are quite out of the question when the atomic weight of copper is concerned; hence, among the many experiments made by me in 1891, only three dealt with material which had been heated above 700°. The evidence of these three experiments (Nos. 59, 81, and 95) is unanimous in showing that most of the occluded impurity is set free at bright redness, and the first two of them agree quantitatively with the results of Dr. Scott.

Although it is thus evident that the English and American results are in no way inconsistent, I decided to repeat a part of the work, in order to obtain a more certain estimate of the various temperatures corresponding to the varying conditions of the cupric oxide. In my previous paper the higher degrees had been merely guessed, for they were not directly concerned in the point then under consideration.

The usual modes of determining high temperatures —the calorimeter, the air-thermometer, the bolometer, the meldometer, the platinum-iridium thermopile, &c.— are somewhat troublesome to use for a brief series of experiments of the present kind, so that it seemed best to determine the several temperatures approximately by finding for each temperature two substances, whose melting-points were respectively above and below the point in question. For instance, an intensity of heat which would melt pure argentic bromide, but not pure argentic chloride, must be between 427° and 451°, a grade of accuracy more than sufficient for the present purpose. This method of determining the temperature has the great advantage of providing an approximate self-registering thermometer, occupying very small space and needing no connection with the outside air. The usefulness of the method obviously depends upon the number of substances easily obtained in a pure state, whose melting-points are accurately known. For such knowledge of high melting-points we depend mainly upon four researches—those of Carnelley (*Journ. Chem. Soc.*, 1876 and 1878, xxix., 489; xxxiii., 273), Le Chatelier (*Bull. Soc. Chim.*, 1887, xlvii., 300), Meyer, Riddle, and Lamb (*Berichte der Deutsch. Chem. Gesell.*, 1895, xxvii., 3129), and Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896 [5], xli., 360). Unfortunately the results of these four investigations do not always agree, their disagreement affording evidence of the great difficulty of measuring accurately high temperatures. At first sight the fact of the existence of such discrepancy might deter one from adopting this standard of reference, but further consideration leads to exactly the opposite conclusion. The melting-points of pure salts must be an unchangeable standard, and the uncertainty of our knowledge regarding them must be largely due to experimental difficulties in the thermometric manipulation. These difficulties, if so serious in researches where everything was favourable to accuracy, must be largely augmented in a research like the present one, in which the temperature could not be made the sole issue of the experiment. Hence the melting-point of a pure salt is the safest possible standard. The following table gives in parallel columns the salts chosen for the present scale of temperature, with the results of the four investigations, and the values of the melting-points selected as the most probable.

The most serious discrepancies are to be noticed in the cases of potassic and sodic chlorides, where the respective averages have been chosen as the most probable values.

Temperature Scale.

	Carnelley Calorimeter.	Le Chatelier Thermopile.	Meyer Air Therm.	Ramsay Meldometer.	Value Selected.
Potassic nitrate ..	339	—	—	339	339
AgI, 2AgBr, 2AgCl	383	—	—	—	383
Argentic bromide	427	—	—	426	427
Argentic chloride	451	—	—	460	451
Plumbic chloride	498	—	—	447	498
Argentic iodide ..	527	—	—	556	527
Sodic biborate ..	561	—	—	—	561
Lithic chloride ..	598	—	—	491	598
Thallous sulphate	632	—	—	—	632
Strontic nitrate..	645	—	—	570	645(?)
Potassic bromide	699	—	722	733	3720
Potassic chloride	734	740	800	762	760
Sodic chloride ..	772	775	815·4	792	790
Sodic carbonate	814	810	849	851	830
Strontic chloride	825	840	832	796	835(?)
Sodic sulphate ..	861	867	863	884	865
Baric chloride ..	860	—	921	844	920(?)
Potassic sulphate	—	1045	1078	1052	1060

These averages are almost identical with the figures obtained by Ramsay and Eumorfopoulos. On the other hand, Joly's meldometer, used by these investigators, seems to have been much less satisfactory at lower temperatures; for their melting-points of plumbic chloride and lithic chloride are widely different from Carnelley's. Repeated qualitative experiments have convinced me that plumbic chloride is less easy to melt than argentic chloride, and lithic chloride less easy to melt than argentic iodide; therefore Carnelley's calorimetric results have been adopted here as the more accurate. Strontic nitrate, and strontic and baric chloride, all begin to decompose in the air at or near their melting-points; undoubtedly this fact is responsible for the very low results obtained by Ramsay and Eumorfopoulos in these cases. Obviously such salts cannot be relied upon as trustworthy thermometers, unless one takes the precautions observed by Meyer, Riddle, and Lamb, in their work with the air thermometer. One is reminded of the interesting work of Hill upon changeable organic melting-points (H. B. Hill, *Proc. Amer. Acad.*, xxiii., 219). The other substances in the list are sufficiently stable, and are easily obtained in a pure state. In the light of Le Chatelier's complete confirmation of Carnelley's results by means of the pyrometric thermopile, it is odd that the lamented Victor Meyer accorded Carnelley so little credit as he has done.

It is needless to state that pains was taken to eliminate impurities from these substances by re-crystallisation or other suitable means, and to dry the salts thoroughly, in the work which follows. If the temperature was below 800°, the dry coarsely powdered substances were contained in small melting-tubes of the hardest Jena glass, sealed while hot at both ends, and sometimes provided with a small platinum sinker to show whether or not the salt had liquefied. If, on the other hand, the height of the temperature excluded glass, the substances were contained in small cups beaten into stout strips of platinum foil. The small amount of impurity taken from the glass tubes in which some of the substances were melted could hardly have had much effect on the melting-points until after a considerable mass of the substances had been melted; but then their mission had been fulfilled.

The table above might well be amplified to cover a wider range, as well as smaller differences of temperature, but such an amplification would constitute a research of some magnitude in itself. For present purposes the above will suffice.

Two forms of apparatus were used for determining the amount and the composition of the occluded gases. The

first was identical in every respect with the most convenient of the three forms described in the original paper (*Proc. Amer. Acad.*, 1891, xxvi., 284). It consists of several bulbs blown in the bend of a glass tube bent at a right angle. One arm of the tube is temporarily closed by a stopcock (not shown in the cut in the original paper, although mentioned in the letterpress), and in this arm the gas, evolved in the bulbs by the solution of the cupric oxide in acid, is collected and measured over boiled water. When necessary the gas may be readily removed through the stopcock at the end of the arm; if a gas burette is attached here, of course the gas may be analysed at once without further trouble.

For most of the experiments, however, Scott's modifications of another of the original forms (*Proc. Amer. Acad.*, xxvi., 285, middle of page) was used. The mode of operating this apparatus was essentially similar to the method just described, although the bent tubes and bulbs are replaced by a small flask and funnel-tube. Scott's addition of a side tube to remove the displaced water distinctly increases the convenience and accuracy of the contrivance. For the details his paper should be consulted.

The two pieces of apparatus give identical results, which cannot be far from the truth. If at all in error the amount of gas collected must be too small rather than too large, for both oxygen and nitrogen are slightly soluble in water. This consideration was verified by fusing a specimen of oxide (another portion of which had been repeatedly analysed in the usual fashion) with carefully prepared acid potassic sulphate in a Sprengel vacuum. The amount of gas evolved by this treatment was slightly greater, but only slightly greater, than the amount obtained by the usual method, and its composition was essentially identical with that of the gas collected over boiled water. Since the question is one of relation, rather than of absolute values, the method involving the use of aqueous solutions was adopted because of its far greater ease of execution. Pains was taken to have the conditions of the solution of the oxide always as nearly as possible the same, so that the results should be strictly comparable with one another.

The first object of the present paper is to show more clearly the relation between the amount of gas retained by the oxide and the temperature used in its ignition. The material employed in these experiments was prepared by dissolving pure copper wire or electrolytic copper in pure nitric acid, and converting by heat the re-crystallised cupric nitrate into basic nitrate and finally into oxide.

(Note.—It is interesting to note that the hydrate of cupric nitrate, which crystallises from hot solutions, probably has the formula $3Cu(NO_3)_2.8H_2O$ (analogous to cadmic sulphate), not $Cu(NO_3)_2.3H_2O$ (Graham), as is usually supposed. Following are the analyses of three separate preparations, dried over moist potash (which does not dehydrate the crystals at ordinary temperatures) proving this point:—

(1) 0·1739 grm. of crystals yielded 0·0471 grm. of copper .. .. =27·08 p.c.
(2) 0·6310 grm. of crystals yielded 0·1705 grm. of copper .. .. =27·01 „
(3) 1·2897 grms. of crystals yielded 0·3448 grm. of copper .. .. =26·73 „

Average =26·94 „

Theoretical value for $Cu(NO_3)_2.3H_2O$=26·20 per cent of copper.
Theoretical value for $3Cu(NO_3)_2.8H_2O$=26·98 per cent of copper.
Theoretical value for $2Cu(NO_3)_2.5H_2O$=27·35 per cent of copper.

The crystals analysed in No. 3 above were large and undoubtedly contained included mother-liquor. Whether or not other hydrates exist, and what the transition temperatures may be, I did not take the trouble to discover. Much of our present data regarding water of crystallisation has been rounded off in the manner indicated above. Undoubtedly many more such irregular ratios as 3 : 8 really exist than we are prepared at present to believe).

Platinum vessels were used throughout, whenever heating was necessary, excepting that one or two of the first ignitions were conducted in a porcelain boat. Three preparations of the oxide were made; one by the rapid decomposition of the nitrate, another by more gradual application of heat, and a third by the very slow action of a temperature just barely sufficient to effect the desired change. This temperature had been previously found by a special experiment to be about 275°, if the products of the decomposition remain in contact with the cupric oxide. The first of these preparations was the most coherent, and was capable of retaining the most gas; the second was less coherent and retained less gas; and the last was the most powdery, and retained even less gas. Thus it is manifest that the physical condition of the solid is a factor in the question.

These specimens of the oxide of copper were subsequently ignited at varying temperatures for varying lengths of time in two different forms of furnace. For the first series a large tube or small muffle of Berlin porcelain

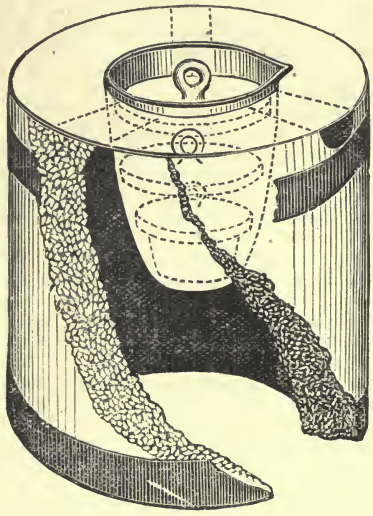


Fig. 1.

capable of being heated to 1200° or more in a Fletcher furnace was used; but since it was found difficult to maintain the tube at a constant temperature throughout, this arrangement was later abandoned. All the subsequent ignitions were performed in a double crucible arranged in the manner shown in the diagram, the low platinum crucible or capsule used to contain the cupric oxide being protected from radiation and convection by a number of superimposed crucible lids. The outer glazed porcelain crucible and the layers of asbestos board covering the draught holes united in excluding the products of combustion of the illuminating gas from the contents of the inner capsule. By means of this furnace, fed with a constant gas supply burning from a fourfold Bunsen burner, a surprisingly constant and uniform temperature may be maintained for an indefinite length of time.

(To be continued).

NOTICES OF BOOKS.

A Text-book of Physiologcal Chemistry. By Olof Hammersten. Authorised Translation from the Author's Enlarged and Revised Third German Edition, by John A. Mandel. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1898. Pp. x.-705. 8vo. Plate.

The author of this treatise, who is Professor of Medical and Physiological Chemistry in the University of Upsala, first published his "Lärobok i fysiologisk kemi och fysiologisk kemisk analys" in 1883. It did not at first attract the attention of students outside of Scandinavia; but after the publication of a second edition, in 1889, it was translated into several languages; a German version appeared in 1891, a Russian in 1892, an Italian in 1893, and the first English version—translated from the German by Professor Mandel—in the same year. The present volume is a translation of the third German edition, no changes or additions having been made except to incorporate Hammersten's Addenda in the text.

The volume of seven hundred large pages is divided into the following chapters:—

I. Introduction. II. Protein substances. III. Carbohydrates. IV. Animal Fats. V. The Animal Cell. VI. The Blood. VII. Chyle, Lymph, Transudations and Exudations. VIII. The Liver. IX. Digestion. X. Tissues of the Connective Substance. XI. Muscle. XII. Brain and Nerves. XIII. Organs of Generation. XIV. Milk. XV. The Urine. XVI. The Skin and its Secretions. XVII. Chemistry of Respiration. XVIII. Metabolism.

The arrangement of the subject-matter was based upon the manner in which physiological chemistry is studied in Sweden, where physiologico- and pathologico-chemical laboratory practice is obligatory on all students of medicine. The analytico-chemical part is distinguished by setting the type without leads, thus making it a handbook for the laboratory.

This volume gives students a most comprehensive survey of the present status of physiological chemistry, and will be found indispensable in the library of every physician who wishes to keep abreast of the times.

Complaint is often made that medical men are not scientific; the researches chronicled in Hammersten's valuable treatise, properly digested, will go far to remove this reproach.

Numerous references to literature and an Index are good features of this admirable work. H. C. B.

A Dictionary of Perfumes used in Soap-making. By A. M. Garance. London: Maclaren and Sons, 37 and 38, Shoe Lane, E.C. Glasgow: 128, Renfield Street.

Soap-makers and perfumers generally will find this book of great use. It being a first attempt at arranging these receipts in dictionary form, the author does not claim completeness, but asks the collaboration of his readers to make it so. We find from this book that a great many perfumes are not even remotely connected with the flower from which they take their names: thus we learn that, although the lily yields a delicate perfume, "in toilet soaps the odour is always imitated"; narcissus, "the odour is imitated by the following mixture," &c.; verbena gives a very fine perfume, "hardly ever used by the perfumer, but a most successful imitation," &c. We are glad to see that English lavender is superior to any other: this is remarkably illustrated by the list of prices of oils of lavender, ranging from one shilling and threepence per pound to six and threepence for that from French picked flowers, while that from Mitcham lavender commands no less than four guineas

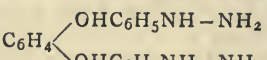
There is a Botanical Appendix at the end, and also a good Index, which add much to the value of the work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

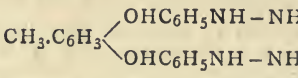
Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 18, October 31, 1898.

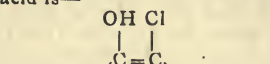
Action of Phenylhydrazin on Chloranilic Acid.—A. Descomps.—By the reaction of phenylhydrazin on phloroglucin in alcoholic solution Baeyer and Kochendœrfer obtained a body corresponding to the formula $C_6H_3(OH)_3(C_6H_5NH-NH_2)_3$. On the other hand, Seyewitz obtained compounds analogous to hydroquinone and orcine, represented respectively by the formulæ—



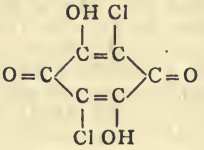
and—



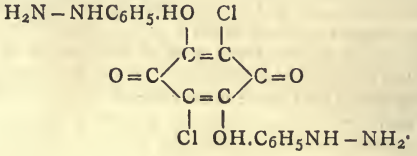
The action of phenylhydrazin on chloranilic acid gave a crystalline body analogous to the above. It has the formula—



The formula ascribed by Kehrmann, Hantsch, and Schniter to chloranilic acid is—



Hence the body obtained by reacting with phenylhydrazin will be represented by—



No. 19, November 7, 1898.

Preparation of Lithium Ammonium, Calcium Ammonium, and the Amides of Lithium and Calcium.—Henri Moissan.—Potassium, sodium, lithium, and calcium combine with ammonia gas, and the ammonium compounds formed decompose at ordinary pressure at the temperature $+70°$ for lithium, $+20°$ for calcium, $-2°$ for potassium, and $-20°$ sodium. Lithium and calcium ammonium take fire in contact with air at ordinary temperatures, and correspond to the formulæ $NH_3.Li$ and $(NH_3)_4Ca$. These two compounds do not dissociate at ordinary pressure and temperature in an atmosphere of ammonia gas. They are stable compounds, which lend themselves to addition and substitution reactions more easily than the ammonium alkalis.

Preliminary Notice of the Presence of Free Hydrogen in Atmospheric Air.—Armand Gautier.—The author has conducted a long series of researches on specimens of air taken from high mountain regions and over the sea. He finds that free hydrogen is present in the proportion of about 1·5 volumes to 10,000 volumes of air. The proportion of hydrogen is considerably greater in the specimens of pure air than in specimens taken from the

neighbourhood of towns, whilst the proportion of combustible carbon compounds is correspondingly less.

Properties of Triethyl Boric Ether.—H. Moissan.—Boron is said to be a trivalent element, capable, like carbon, of combining with itself, and by condensation, a partial dehydration of its fundamental hydrate, $B(OH)_3$, forming new hydrates to an indefinite extent; *e.g.*—

$$\begin{array}{lll} B(OH)_3, & B_2H_4O_5, & B_3H_5O_7 \ldots. \\ BO_2H, & B_2H_2O_4, & B_3H_3O_6 \ldots. \\ & B_2O_3, & B_3HO_5 \ldots. \end{array}$$

Hence, theoretically, the number of corresponding ethers is also unlimited. But, in fact, only two classes of boric ethers are known, viz., the tri-alcoholic, BO_3R_3, and the mono-alcoholic, BO_2R (discovered by Ebelmen in 1846, and investigated by Schiff in 1867). The former are liquid bodies, capable of distillation, and of definite composition; the latter have yielded no consistent results on analysis, and are incapable of distillation and crystallisation. To complete the study of the tri-alcoholic borates, the author of this paper has chosen the case of the triethyl borate, $BO_3(C_2H_5)_3$. It was prepared according to Schiff's method, by the direct action of B_2O_3 on absolute alcohol at 120° (under a pressure of about 2 atmospheres). $B_2O_3+3C_2H_5OH=BO_3(C_2H_5)_3+BO_3H_3$, triethyl borate, is a mobile, colourless liquid, of density 0·887 at 0°, boiling at 119·5°, and a non-conductor of electricity; it is immediately saponified by water, and of all the anhydrous reagents with which it was treated, chlorine, alkaline ethylates, and alkalis, alone gave definite results. Chlorine replaced the hydrogen of ethyl borate, giving at the end of the reaction a gelatinous mass. The increase of weight indicated the entrance of five chlorine atoms into 1 molecule of $BO_3(C_2H_5)_3$. On treating with potash an oil was obtained which partially decomposed on distillation, and possesses the formula $C_4H_7Cl_3O$, or—

$$\begin{matrix} CHCl_2.CHCl \\ C_2H_5 \end{matrix}\!\!>\!O.$$

On treating triethylborate with sodium alcoholate, dissolved in absolute alcohol, a white crystalline powder was finally obtained, possessing the formula—

$$BO_3(C_2H_5)_3+C_2H_5ONa.$$

This compound is easily decomposed by water, but can be heated to 200° without decomposition; it demonstrates the pentavalence of boron.

Combinations of Phenylhydrazin with the Halogen Salts of the Alkaline-earth Metals.—J. Moitessier.—With anhydrous calcium chloride, dissolved in alcohol, phenylhydrazin yields the stable compound—

$$CaCl_2.2(C_6H_5NH{\cdot}NH_2),$$

crystallising on cooling. Anhydrous strontium chloride reacts similarly, but the combination is easily decomposed by the ordinary solvents. Phenylhydrazin calcium bromide, $CaBr_2.4(C_6H_5NH{\cdot}NH_2)3H_2O$, was obtained by adding the theoretical quantity of phenylhydrazin to calcium bromide dissolved in water, and evaporating the solution. Crystals are obtained, soluble in alcohol, and decomposed by boiling benzene. Anhydrous strontium bromide also combines with phenylhydrazin, 1 molecule of the former to 2 molecules of the latter. A hydrated combination can also be obtained. The iodide, $SrI_2.4(C_6H_5NH{-}NH_2)$, is similarly prepared, and consists of deliquescent prismatic crystals. Phenylhydrazin does not combine with the fluorides of the alkaline earths, but such combinations are possible with certain fluorides of the magnesium group, notably zinc fluoride. It also combines with cuprous salts, with lithium bromide, and with oxalates and benzoates of the magnesium group.

Estimation of Gelatin in Gums and Food Substances.—A. Trillat.—It is known that formaldehyd, when heated with albumenoid substances, renders the latter insoluble, and this property may be utilised for detecting and estimating the gelatin fraudulently added to gums and food substances. A description of the process is given as applied to the case of gum arabic. It is easily possible, by means of this process, to distinguish artificial jellies from gelatin and natural vegetable jellies.

No. 20, November 14, 1898.

The Preparation of Crystalline Tungsten by Electrolysis.—A. Hallopeau.—The author obtains crystalline tungsten by electrolysing paratungstate of lithium. He uses platinum electrodes, and passes a current for three hours. At the end of that time the resulting mass is repeated, treated with boiling water, then with strong hydrochloric acid, and lastly with a boiling lithia solution. At the end of these washings there remains a crystalline substance consisting of tungsten mixed with a certain quantity of platinum from the electrodes. The tungsten is found in opaque crystals, usually in the form of needles. The composition of these crystals is proved by analysis.

Volumetric Estimation of Boric Acid.—M. Copaux.—The author refers to a former paper in which is given the preparation of certain boric compounds. The present paper treats of the mode of analysis of the same compounds. It is found that though the volumetric estimation of free boric acid titrated with an alkali is an impracticable method, yet the acid can be estimated volumetrically as follows:—The weighed material dissolved in a small volume of water, coloured yellow by two drops of helianthine, then saturated with sulphuric or hydrochloric acid till the solution is red. The boric acid is now displaced by a strong acid, and if a known volume of glycerin is added the solution can be titrated against soda solution, phenolphthalein being used as an indicator.

New Halogen Derivatives of Guaiacol and Veratrol.—H. Cousin.—The author discusses the preparation and properties of the following new bodies:—Trichlor-guaiacol, trichlor-veratrol, dibrom-guaiacol, tetrabrom-guaiacol, and tribrom-veratrol.

A New Sugar accompanying Sorbite.—Camille Vincent and J. Meunier.—Examination of the mother-liquors from the preparation of sorbite from certain fruits, led the authors to the discovery of a homologous body capable, like sorbite, of combining with benzaldehyd. This new alcohol is octatomic, having crystalline derivatives, itself, however, only having been obtained as a syrup. The sorbite solution is concentrated, to effect deposition of the crystals of sorbite, the non-crystallisable mother-liquor treated with the sorbose bacterium for conversion of any remaining sorbite, and, finally, the unchanged liquid treated with benzaldehyd in presence of sulphuric acid, and thus the new alcohol isolated as an acetal. The latter crystallises from chloroform, therein differing from the acetal of sorbite, which is not crystalline. Analysis gives it the formula of the dibenzoic acetal of an alcohol, $C_8H_{18}O_8$.

Derivatives of Natural Methyl-heptenone.—Georges Leser.—Not suitable for abstraction.

Volumetric Estimation of Ethyl-aldehyd.—X. Rocques.—The author makes an addition to his recent paper on the estimation of ethyl-aldehyd by means of acid sulphites, to the effect that temperature exercises a considerable influence on the reaction. At a temperature of from 25° to 30° the reaction is complete in less than twenty-four hours, whilst at 15° it is not complete after a lapse of forty-eight hours.

Method of Formation of Indigo in the Industrial Processes of Extraction. Diastasic Functions of the Indigofera.—L. Bréandat.—For investigation of the ferment by means of which indigo is obtained from the glucoside indican contained in the Indigofera and other plants, the author took the case of *Isatis alpina*. The results of treating the leaves of this plant in various ways pointed to the following conclusions:—(1) The micro-organisms play no conspicuous part in the fermentation,

(2) This plant contains a hydrating and oxidising diastase, the former converting the indican into indigo-white and indiglucine, the latter oxidising the indigo-white to indigo-blue. (3) All plants capable of yielding indigo contain these two diastases.

———

Journal de Pharmacie et de Chimie, vol. viii., No. 3.

The Enamel of Cooking Utensils.—L. Barthe.—In a recent case of poisoning, by which one person lost his life and several others were made very ill, the poison was said to be traced to an enamelled iron saucepan of the familiar kind, white inside and deep blue outside. Some French enamels have been found to contain as much as 52·51 per cent of oxide of lead and 3·74 per cent of arsenic acid. The enamelled utensil in question, however, did not contain either of these, but did contain large proportions of silica, tin, and aluminium, small quantities of zinc, lime, and potash, and traces of iron and cobalt; the author is therefore of the opinion that in this case the enamel was not to blame.

Estimation of Boric Acid.—M. Vadam. —Already inserted.

No. 4.

The Action of Soluble Ferments on the Pectic Products of Gentian Root.—E. Bourquelot and H. H. Hérissey.—The authors have already shown that there is a certain analogy between the hydration by warm water of the principle of gentian which furnishes pectine, and that of starch. They have also shown that the pectine of this plant, submitted to the hydrolysing action of dilute warm sulphuric acid, gives a reducing sugar—arabinose. They now describe experiments to determtne whether there are not existing soluble ferments capable of acting on pectose or pectine, and they find that *Aspergillus niger* has a hydrating action on pectose: this action is confirmed by several experiments in the case of pectine; all the experiments with *Aspergillus* and with saliva gave negative results.

MISCELLANEOUS.

Illustrated Catalogue of Scientific Apparatus, issued by Messrs. W. and J. George, Lim.—We have received a complete Illustrated Catalogue of Scientific Apparatus from Messrs. W. and J. George, Limited, who have taken over the business formerly carried on by F. E. Becker and Co., of Hatton Wall, E.C. It includes many new and recently devised pieces of apparatus which will be welcome to chemists. The illustrations are particularly good and numerous. Among the novelties are a series of torsion balances, ranging from a chemical balance to turn with a hundredth of a grain, to druggists' scales with a load capacity of twenty pounds. This form of balance has been very little used in England, and is likely to prove of value, especially where it is exposed to rough usage. Lovibond's tintometer, with its many adaptations; a complete series of hot-air engines and turbines, from 1-60th of a horse-power and upwards, with a great many pieces of apparatus for rocking, shaking, stirring, &c.; Röntgen's apparatus and Wimshurst machines. Crookes's tubes, and apparatus for illustrating Tesla's, Hertz's, and Marconi's experiments, are also described. The section devoted to bacteriological apparatus is complete, and contains some of the latest additions. With the chemical apparatus are included many new items; among others we note the long-wished-for steel tube cork-borer. A special point is made of an efficient chemical balance with agate knife edges and bearings sensitive to 1 m.grm., at a price which places it within the reach of any student. Chemists and physicists generally will be grateful to Messrs. George and Co. for having placed in their hands such a complete list of apparatus.

MEETINGS FOR THE WEEK.

Monday, 16th.—Society of Arts, 8 (Cantor Lectures). "Bacterial Purification of Sewage," by Dr. Samuel Rideal.

Tuesday, 17th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

Wednesday, 18th.—Society of Arts, 8. "Canals and Inland Navigation in the United Kingdom," by L. F. Vernon-Harcourt, M.A.

—— Institution of Mining and Metallurgy, 8. "The Tin Mines of Bolivia," communicated by W. McDermott. "On Minerals found in the Silver Lodes of Tatasi, and Portugalete, Bolivia," by Malcolm Roberts. "The Deep Leads of Victoria," by E. Lidgey. "Notes on Blue Asbestos," by H. F. Olds. "Notes on Dry Crushing on the Witwatersrand," by Franklin White.

Thursday, 19th.—Chemical, 8. "Researches on Moorland Waters—I. Acidity," by W. Ackroyd. "α-Ketotetrahydronaphthalene," by Dr. S. Kipping, F.R.S., and Alfred Hill. "A New Method for Preparing *as.*-Dimethyl- and Trimethyl-succinic Acids," by W. A. Bone. "Reduction of Optically Active Mono- and Di-alkyloxysuccinic Acids from Malic and Tartaric Acids," by T. Purdie, F.R.S., and W. Pitheathly, B.Sc. "Action of Ammonia on Ethereal Salts of Organic Bases," by S. Ruhemann, M.A., Ph.D. "Esterification Constants of Substituted Acetic Acids," by J. J. Sudborough, Ph.D., and L. L. Lloyd. "Di-ortho-substituted Benzoic Acids—Part IV., Formation of Salts from Di-ortho-substituted Benzoic Acids and different Organic Bases," by L. L. Lloyd and J. J. Sudborough, Ph.D. "The Thermal Effects of Dilution," by J. H. Pollok. "The Changes of Volume due to Dilution of Aqueous Solutions," by F. B. H. Wade, B. A.

—— Royal Institution, 3. "Tibet and the Tibetans," by A. Henry Savage Landor.

—— Society of Arts, 4.30. "Railways in Burma and their Proposed Extension across Yunnan," by J. Nisbet. (This Meeting will be held at the Imperial Institute).

Friday, 20th.—Royal Institution, 9. "Liquid Hydrogen," by Prof. Dewar, M.A., LL.D., F.R.S.

Saturday, 21st.—Royal Institution, 3. "Liszt" (with Musical Illustrations), by Sir Alexander C. Mackenzie, Mus. Doc.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2043.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

By F. W. DAW, Assoc. R.C.S., F.I.C., F.C.S.

The permanganate method of estimating manganese, although a rapid and simple method, is very generally ignored, and in some cases is held in bad repute. The cause for this perhaps is to be found in the fact that under certain conditions inconsistent results can be easily obtained. The sources of error when working on ferro and spiegel are chiefly due to three causes: firstly, non-elimination of the organic matter present; secondly, reckless addition of ZnO in large excess and in hot solutions; and thirdly, standardising the permanganate with iron instead of manganese.

To eliminate these errors I have adopted the following method, which I find gives very concordant results:—0·5 grm. of ferro or spiegel is weighed out and introduced into a wide-mouth 16 oz. Phillips beaker, and in the case of ferro 0·4 grm. of pure iron wire is added, to render the precipitation by oxide of zinc easier. The ferro or spiegel is dissolved in 30 c.c. HCl, and the iron oxidised with a few c.c. HNO_3, 15 c.c. of 50 per cent H_2SO_4 is then added, and the whole evaporated on the hot plate till fumes of H_2SO_4 are copiously evolved. When cool, water is added, the sulphates dissolved, and the solution washed out into a 1000 c.c. conical flask. Cold water is added to make up to about 500 c.c., the acid partially neutralised with Na_2CO_3, and oxide of zinc gradually added till the iron is all precipipitated, but a large excess of zinc is to be avoided. The solution containing the precipitate is without filtering brought to a boil, and standard permanganate run in till within a few c.c. of the expected amount; the flask is well shaken, and the permanganate run in, a few drops at a time, till a pink colour appears above the precipitate. This is easily observed by holding the flask on one side, covering the mouth of flask with a cloth, and waiting a few seconds till precipitate is partially settled, when a pink colour is easily seen near the neck.

The standard permanganate solution is made up by dissolving 10 grms. $K_2Mn_2O_8$ to a litre of water, and standardising it by means of ferro-manganese of known composition.

If iron is used to standardise the solution, a figure is obtained which gives low results when working on manganese. Brearley (Chem. News, lxxv., p. 15) considers this due to a small amount of carbon in the iron wire used, but the same result is found if pure ferrous ammonium sulphate is used containing no carbon.

The estimation of the manganese in the standard ferro I make by weighing as Mn_3O_4 after precipitation by bromine and ammonia. This is a method which has received a large amount of adverse criticism, but which gives very good results if worked properly. The precipitate after drying is ignited (the paper being burnt first) in a platinum crucible over the full blast of the blowpipe for three or four minutes. The precipitate after weighing is freed from silica, oxides of iron, copper, nickel, &c., by dissolving in HCl, diluting, adding ammonium acetate, passing H_2S, and filtering; this is ignited, weighed, and subtracted from the total precipitate.

The volumetric method described by Brearley (Chem. News, lxxv., p. 15) gives very fair results, but is, I think, needlessly complicated. The separation of iron and manganese by a minimum amount of sodium acetate, described there, gives a very perfect separation, not a trace being found on testing the acetate precipitate.

THE ANALYSIS OF MANTLES FOR INCANDESCENT GAS BURNERS.

By E. HINTZ.

The commercial incandescent mantles of to-day are composed almost entirely of oxide of thorium, ThO_2, to which has been added a small quantity of oxide of cerium, CeO_2, varying from 0·5 to 2·0 per cent. With the exception of a small quantity of lime they only contain traces of impurities, such as nitrate of thorium, and oxides of zirconium, neodymium, lanthanum, and yttrium. The estimation of all these bodies is an extremely delicate operation. To satisfy himself that these impurities have no appreciable influence on the luminous power of the mantle, and therefore that not much notice need be taken of these impurities in the analysis of incandescent bodies, the author has undertaken a series of photometric measurements, from which he has been able to establish the following conclusions:—

1. The oxides of zirconium, lanthanum, and yttrium up to 1 per cent do not increase the illuminating power of mantles composed of pure oxide of thorium. Oxide of neodymium increases it to a slight extent. With a consumption of 111 litres of gas per hour, the addition of 1 per cent of this oxide increases the illuminating power by 13 Hefner candles.

2. The admixture of 1 per cent of oxide of neodymium, lanthanum, or yttrium, and the addition of 0·2 to 1·0 per cent of oxide of zirconium, have no influence on the illuminating power of mantles made from thorium. The influence of 2·0 per cent of oxide of zirconium is doubtful.

3. The admixture of 1 per cent of the oxides of zirconium, neodymium, lanthanum, or yttrium has no influence on the emissive power of thorium-cerium mantles containing 0·5 per cent of lime. The lime contained in the mantles doubtless comes from the ash of the tissue used in their manufacture. It is this substance which increases the fragility of the mantles, and it should always be eliminated as far as possible.

In collaboration with H. Weber, the author has examined Knorre's method for the estimation of cerium; it is well known that this method consists in acidulating the solution of the cerous salt by sulphuric acid, and transforming it into ceric salt by boiling in presence of persulphate of ammonium. The yellow ceric compound is reduced by dilute peroxide of hydrogen to the state of a colourless cerous salt, and the excess of peroxide of hydrogen is titrated by means of permanganate. Ten atoms Fe=2 molecules $KMnO_4$=5 molecules H_2O_2=10 molecules CeO_2; consequently 56 parts Fe = 140 parts Ce = 172 parts CeO_2. To oxidise 0·2 to 0·3 grm. of cerium it suffices to use 3 grms. of persulphate of ammonium. This method applied to the analysis of thorium-cerium mantles gives good results when carried out *exactly* in the following manner.

The solution (see further on) containing about 1 grm. of ThO_2 and 0·01 grm. of CeO_2 is acidulated with 5 to 7·5 c.c. of dilute sulphuric acid (1 vol. H_2SO_4+6 vols. H_2O); it is diluted up to 200 c.c., and a part only of the persulphate of ammonium added. It is then heated to boiling for two minutes, cooled to 40—60° C., and a second portion of the persulphate of ammonium added. After a second boiling, followed by a second cooling, the remainder of the persulphate is added, and the whole boiled for ten or fifteen minutes.

Towards the end of the ebullition we add a further 2 c.c. of dilute sulphuric acid, and then cool completely, after which, by means of a burette, dilute peroxide of

hydrogen is added drop by drop, until the yellow colouration disappears; we then immediately titrate the excess of peroxide of hydrogen by means of a solution of permanganate.

The presence of nitrates in small quantities does not interfere with the results; but acidification by nitric acid instead of sulphuric acid would lead to too low results.

The simplified method for the analysis of incandescent mantles, proposed by the author, is as follows:—

Take at least twelve mantles *before incineration*, cut off the upper and lower extremities, keeping only the middle portions, for the upper parts are frequently impregnated with hardening substance, and the lower parts are likely to contain an excessive proportion of nitrate of cerium. Weigh the middle parts, and thoroughly exhaust them with water to which a few drops of nitric acid have been added. Burn the tissue, melt the residue with bisulphate of potassium, take up with dilute hydrochloric acid, precipitate with ammonia, dissolve the precipitate in nitric acid, add the solution thus obtained to the principal solution, and dilute to a convenient bulk.

1st. We can detect the presence of 1 part of oxide of neodymium Nd_2O_3 in 100 parts of oxide of thorium in a portion of the liquid by its characteristic colour, and by the absorption bands observed in the spectroscope.

2nd. Precipitate part of the solution with oxalic acid, after having eliminated the excess of mineral acid by evaporation. Collect the precipitate (*a*) on a filter of hard paper, transfer this precipitate to a beaker, heat with a concentrated solution of oxalate of ammonia, dilute with water, allow to cool, filter again after the solution has been standing for a considerable time, calcine and weigh.

The precipitate may contain a small quantity of thorium, so that even in the absence of neodymium, lanthanum, and yttrium the result in oxide of cerium will be a little too high. At the same time the presence of lime affects the accuracy of the results in the same manner. In any case if the weight of the precipitate does not exceed the actual weight of the oxide of cerium by more than 1 per cent, we may safely assume that the mantles do not contain either lanthanum, neodymium, or yttrium in appreciable quantities. If the divergence is greater than 1 per cent the precipitate should be re-dissolved in sulphuric acid, and submitted to complete analysis for the detection and estimation of the earths.

To test the filtered liquid from (*a*) for oxide of zirconium we evaporate to dryness, calcine gently, re-dissolve in hydrochloric acid, evaporate off the excess of acid, and run the residue on to a glass plate by means of a few drops of water. Drive off this water by evaporation, then add a drop of water and a drop of binoxalate of potassium, evaporate to dryness again, and search under the microscope for the characteristic crystals of the double oxalate of potash and zirconium. The presence of 0·1 per cent of oxide of zirconium can be recognised by the method we have just described, even when working on only one mantle.

3rd. Evaporate off the excess of acid in a part of the solution, and precipitate with oxalic acid; calcine and weigh the precipitate which contains all the rare earths, with the exception of oxide of zirconium. The results are influenced by lime. But with mantles formed of 1·2 per cent CeO_2, 98·4 per cent ThO_2, and 0·4 per cent CaO, there is no particular disadvantage in considering lime as oxide of thorium.

4th. Titrate the cerium in a known volume of the solution by Knorre's method, remembering that the presence of a small quantity of organic matter, resulting from the exhaustion by nitric acid, will necessitate the use of a slightly larger quantity of persulphate of ammonia to that indicated above. In the absence of neodymium, lanthanum, and yttrium, or in the presence of only small quantities of these bodies, the difference between the results of (4) and (3) will give the oxide of thorium.—*Zeit. Anal. Chem.*, xxxvii. [2], p. 94.

ON THE USE OF OXALATE OF SODA IN VOLUMETRIC ESTIMATIONS.

By P. L. SÖRENSEN.

The author recommends the use of normal oxalate of soda to form carbonate of soda, for determining the titration value of the normal acids used in volumetric estimations.

The pure product can be prepared in the following manner:—

One part of commercial oxalate of soda is dissolved in 32 parts of water: this makes a saturated solution at 15° C. The solution is made slightly alkaline by means of caustic soda; it is then left in a large beaker until it becomes perfectly limpid. It is then filtered to separate any impurities which may not have dissolved, notably oxalate of lime. The clear solution is evaporated to one-tenth of its original volume on a water-bath. The oxalate of soda crystallises, and the mother-liquor contains the greater part of the most soluble impurities, such as oxalate of potash, caustic soda, the alkaline chlorides and sulphates, &c. The crystals of oxalate of soda are filtered off, crushed, and washed several times with cold water. A second crystallisation enables us to obtain the salt in an altogether pure state.

Oxalate of soda does not contain any water of crystallisation; it can be heated to 125—150° without undergoing decomposition. It is not hygroscopic, and can be weighed with great accuracy. A given weight of oxalate of soda can be transformed into carbonate for the purposes of analysis by simple calcination in a platinum crucible furnished with a tightly-fitting cover to prevent losses by projection. If a little carbon is formed it can be burnt away by partially uncovering the crucible towards the end of the operation.—*Zeitschr. Anal. Chem.*, xxxvi., p. 639.

A VOLUMETRIC METHOD FOR THE ESTIMATION OF GRAPE SUGAR, MILK SUGAR, AND OTHER BODIES CAPABLE OF REDUCING FEHLING'S SOLUTION.

By E. REIGLER.

This method is based on the estimation of the copper in a known volume of Fehling's solution, before and after reduction. The determination is carried out by means of Haen's iodometric method.

The cupric solution is prepared by dissolving 34·64 grms. of crystallised sulphate of copper in 500 c.c. of water. The solution of Seignette salt is prepared by dissolving 175 grms. of this salt and 50 grms. of sodic hydrate in 500 c.c. of water.

To titrate the cupric solution (once for all) we pour 10 c.c. of each of the above-mentioned solutions into a flask of 200 c.c. capacity, add 100 c.c. of water, 2 c.c. of pure concentrated sulphuric acid, and stir the whole carefully. We then add 1 grm. of iodide of potassium dissolved in 10 c.c. of water, shake, and allow to stand for ten minutes. We finally add 3 c.c. of starch solution, and titrate the iodine set free by means of decinormal hyposulphite, until the blue colour disappears and does not reappear until after the lapse of five minutes. If the colour comes back after this interval, no notice need be taken of it.

From the equation $2CuSO_4+4KI=2K_2SO_4+Cu_2I_2+I_2$, it follows that each c.c. of the hyposulphite solution represents 0·00635 grm. of copper. If the solutions are properly prepared 10 c.c. of the cupric solution will require 27·8 c.c. of the hyposulphite solution, corresponding to 0·1765 grm. of copper.

For the estimation of grape sugar we add together 10 c.c. of the cupric solution, 10 c.c. of the Seignette solution, and 30 c.c. of water, in a flask of about 200 c.c. capacity. The whole is heated to boiling, and then, by means of a pipette, exactly 10 c.c. of the solution of sugar is added; this solution should not contain more than 1 per cent. The boiling is kept up for a few seconds. The precipitate is allowed to settle, which does not take long; then filter and wash with 80 c.c. of water. The filtrate is received in a 200 c.c. flask, and titrated as described above. If v be the number of c.c. of hyposulphite used, the quantity of copper reduced by the sugar will be $(27{\cdot}8-v)$ 0·00635.

The corresponding amount of sugar can then be calculated by means of Allen's tables.

Before estimating the milk sugar in milk it is necessary to remove the albumenoid matter; this is easily and completely done by means of asaprol. To 500 c.c. of water we add 15 grms. of asaprol and 15 grms. of crystallised citric acid, and filter the solution. Of this solution, which will keep indefinitely, we take 15 c.c. and add them to 10 c.c. of milk in a flask of 100 c.c. capacity, and make the volume up to the mark on the flask with distilled water. The mixture should be vigorously shaken, heated to 60°, and filtered: 20 c.c. of the clear liquid are boiled for six minutes with 10 c.c. of the cupric solution, 10 c.c. of the Seignette solution, and about 30 c.c. of water, in a flask of 200 c.c. capacity. After filtering and titrating, the formula $(27{\cdot}8-v)$ 0·00635 will give the quantity of copper reduced, and Soxhlet's table will give the corresponding amount of milk sugar present. In actual work the quantity found is expressed for 2 c.c. of milk. If the quantity of copper reduced is less than 100 m.grms., we can, without appreciable error, consider that each m.grm. of copper corresponds with 0·725 m·grm. of milk sugar.

The precipitate collected on the filter may be used for estimating the fat and the total nitrogen.—*Zeit. Anal. Chem.*, 1892, xxxvii. [1], p. 22.

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 21).

In the following table are given the new series of results showing the relation of the total volume of gas retained to the temperature used in the ignition of the cupric oxide. The gas volumes are reduced to 0° and 760 m.m. pressure, the reduction having been made by means of a Winkler-Lunge corrector arranged to give directly the exact volume of a mass of moist air which would measure 100 c.c. when dry and under standard conditions.

The Effect of Temperature on the Total Amount of Gas occluded by Cupric Oxide.

First Series: First Preparation of Cupric Oxide.

		C.c. gas.
1.	1 grm. CuO, heated 1 hour at 300°±, (*a*) gave	0·18
2.	,, ,, ,, ,,	0·19
3.	,, ,, ,, ,,	0·21
	Average	0·19
4.	1 grm. CuO, heated 4 hours at 500°±, (*b*) gave	0·69
5.	,, ,, ,, ,,	0·72
	Average	0·70
6.	1 grm. CuO, heated 1 hour at 830°±, (*c*) gave	0·68
7.	,, ,, ,, ,,	0·69
8.	,, ,, ,, ,,	0·68
	Average	0·68
9.	1 grm. CuO, heated ½ hour at 870°±, (*d*) gave	0·55
10.	,, ,, at 900°±, (*e*) ,,	0·08
11.	,, ,, at 950°±, (*f*) ,,	0·05
12.	,, ,, ,, ,,	0·04
	Average	0·05
13.	1 grm. CuO, heated ½ hour at 1100°±, (*g*) gave	0·01(?)

Second Series: Second Preparation of Cupric Oxide.

14.	1 grm. CuO, heated 4 hours at 280°±, (*h*) gave	0·04
15.	,, 1 hour at 290°±, (*h*) ,,	0·12
16.	,, 5 hours at 630°±, (*i*) ,,	0·54
17.	,, 3 hours at 830°±, (*j*) ,,	0·57
18.	,, ,, ,, ,,	0·59
19.	,, 5 hours ,, ,,	0·57
	Average	0·58
20.	1 grm. CuO, heated 20 mins. at 870°±, (*j*) gave	0·42
21.	,, 150 ,, ,, ,,	0·23
22.	,, ,, ,, ,, ,,	0·14
23.	1 grm. CuO, heated 2 hours at 950°±, (*j*) gave	0·04
24.	,, ,, ,, ,,	0·07
25.	,, ,, ,, ,,	0·04
	Average	0·05

(*a*) Mercury thermometer.
(*b*) Plumbic chloride just fused; argentic iodide remained solid.
(*c*) Sodic chloride easily fused; strontic chloride just fused; sodic sulphate remained solid.
(*d*) Sodic sulphate just fused.
(*e*) Sodic sulphate easily fused; higher than last.
(*f*) Baric chloride easily fused; potassic sulphate remained solid.
(*g*) Potassic sulphate fused, as well as the cupric oxide itself.
(*h*) Mercury thermometer.
(*i*) Thallous sulphate just melted.
(*j*) See footnotes to preceding series for criteria regarding temperatures 830°, 870°, and 950°.

These two series of experiments, qualitatively and quantitatively similar to those carried out in 1891, lead to the following conclusions, which are copied verbatim from the paper on the atomic weight of copper:—

"First, *that cupric oxide prepared by the ignition of the oxynitrate after Hampe's method contained between four and five times its volume of occluded gas.*

"Second, *that ignition of the oxide at very bright redness was capable of expelling a portion of this gas. The temperature required was nevertheless considerably above that which Hampe apparently employed.*"

The recent experiments add to these conclusions only greater definiteness. It is now clear that nearly all the gas is retained until a temperature of slightly over 860° is reached, when more than nine-tenths of it is rapidly set free. Somewhat above this point the cupric oxide is itself partly decomposed; and in the neighbourhood of 1000° the mixture of cupric and cuprous oxides fuses first into a mass resembling scoria, and then into a limpid fluid. It is evident that Scott must have used in his muffle a temperature somewhere between 850° and 1000°, for he found on the average 0·055 c.c. of gas per grm. of cupric oxide, while my results obtained by means of temperatures in this neighbourhood average 0·05 c.c. Moreover, some of his material was slightly reduced, but apparently none of it was melted.

It was clearly shown in the previous papers that the low results given by material ignited at temperatures

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 22; also *American Chemical Journal*, November, 1898.

below 450° are due to the presence of undecomposed cupric nitrate, which by its decomposition at higher temperatures yields the gas forming the subject of the present discussion.

The fact that prolonged ignition does not affect the amount of gas occluded, may be inferred from the experiments just recorded; but in order to obtain more definite information on this influence of time, a third series of experiments was made.

The Effect of Time of Ignition on the Total Amount of Gas occluded by Cupric Oxide.

Temperature: The Fusing-point of Thallous Sulphate, about 640°.

		C.c. gas.
26.	1 grm. of CuO, after ignition for 10 mins., gave	0·56
27.	,, ,, ,,	0·57
28.	,, ,, ,,	0·53
	Average	0·55
29.	1 grm. of CuO, after ignition for 5 hours, gave	0·56
30.	,, ,, ,,	0·59
	Average	0·57
31.	1 grm. of CuO, after ignition for 20 hours, gave	0·56
32.	,, ,, ,,	0·59
	Average	0·57

A portion of the last specimen, which had been heated for twenty hours, was further ignited for five hours at about the fusing-point of common salt (about 800°). Upon solution in acid this portion yielded the same amount, 0·59 c.c. of gas. Thus another of the conclusions arrived at in 1892 is confirmed:—

"Third, *that beyond a certain limit the time of ignition makes no important difference.*"

This is true, however, only below 850°. Experiments 20 to 22 show that when the imprisoned gas has once begun to be set free, at temperatures above 850°, the time is an essential factor, and that when sufficient time has been allowed the expulsion of the gas is almost complete. Scott examined only cupric oxide from which he had thus expelled the gas.

In this connection it is interesting to note that Morse and Arbuckle (*Amer. Chem. Journ.*, xx., 195) have recently verified, with apparatus far more elaborate and exact than ours, the results of Rogers and myself, concerning the amount of gas occluded by the oxide of zinc (*Proc. Amer. Acad.*, xxviii., 200). Considering the fact that the manner of preparation of the substance undoubtedly affects the amount of gas retained, the closeness of the agreement is surprising. Only one of their conclusions is different from ours: in their opinion there is no reason to believe that the temperature of ignition of the oxide has any effect on the composition of the occluded gas, while in our experiments the imprisoned oxygen decreased with increasing temperature. The basis of their reasoning is the supposition that the total amount of gas retained is dependent solely upon the temperature; using this total amount as a thermometer, they point out the fact that the smaller amounts of gas obtained in their experiments did not always contain the smaller amounts of oxygen; and hence they conclude that the temperature is not an essential determining cause of the composition of the mixture. In a letter answering some questions about the matter, Professor Morse kindly writes:—"We made every effort to secure constant temperatures for our oxide, giving the closest attention, to that end, to every detail of the firing of the furnace, the fuel, the location of the crucibles," &c. Since this is the case, and I cannot doubt the essential success of their efforts, it seems to me that their results have but little bearing upon the effect of *varying* temperatures on the oxide. The fact that their mixture of gases was by no means constant in composition is better explained by the supposition that some other cause besides the temperature influences the relation of the volumes of oxygen and nitrogen retained, or else that the total amount of the enclosed gases is not a safe measure of the temperature. It will be shown that both of these inferences are correct, and hence that the logic of Morse and Arbuckle's point, correct in itself but unsafe in its premises, falls to the ground.

A careful study of all the data, Morse and Arbuckle's as well as ours, convinced me that, while the two gases must be evolved together, they behave subsequently in quite a different fashion. It is apparent immediately that the oxygen must escape at first much faster than the nitrogen, for the ratio of the two volumes in the nitric anhydride set free must be originally 5 : 2, while the average of Morse and Arbuckle's result showed that less than a fifth of the finally retained mixture consisted of oxygen. Part of the loss might be due to the preliminary formation of lower oxides, and to unequal diffusion, but this cannot account for so great a loss of oxygen. Even nitrous oxide should yield upon decomposition a mixture one-third of the volume of which must consist of oxygen; and the fractional diffusion of this mechanically enclosed mixture should allow the lighter of its two constituents, nitrogen, to escape the more quickly of the two; hence the mixture should contain never less than 33 per cent of oxygen. The same anomaly is even more manifest in the case of cupric oxide, for from this substance nearly all the oxygen soon escapes even at comparatively low temperatures.

Why then does the oxygen escape the more easily of the two gases? This question introduces us at once to the second section of the paper, which deals with the composition of the occluded gases.

The first step toward answering the question is a certain determination of the facts, which have been doubted by Morse and Arbuckle. The three conditions which would be most likely to affect the amount and composition of the gaseous mixture are the temperature of ignition, the time of ignition, and the compactness of the solid material. In order to test the effect of these possible modifying causes experimentally, several series of analyses were made, both with zincic and with cupric oxide.

The zincic oxide was made by heating pure zincic nitrate for a long time at 280°. It was more compact than the cupric oxide, and undoubtedly contained residual traces of nitrate until further ignited.

The Effect of Temperature on the Total Volume of Gas occluded by Zincic Oxide.

First Series: Heated Three Hours.

		C.c. gas.
34.	1 grm. of ZnO, after heating 3 hrs. at 660°± gave	0·365
35.	,, ,, ,, ,,	0·380
	Average	0·373
36.	1 grm. of ZnO, after heating 3 hrs. at 750°± gave	0·233
37.	,, ,, ,, ,,	0·210
	Average	0·221
38.	1 grm. of ZnO, after heating 3 hrs. at 880°± gave	0·14
39.	,, ,, ,, ,,	0·18
	Average	0·16

Second Series: Heated Thirty Minutes.

40.	1 grm. of ZnO, after heating ½ hr. at 750°± gave	0·366
41.	,, ,, ,, ,,	0·320
	Average	0·343
42.	1 grm. of ZnO, after heating ½ hr. at 880°± gave	0192
43.	,, ,, ,, ,,	0·192
	Average	0·192

Evidently, other conditions being equal, the total amount of gas retained decreases very considerably as the temperature of ignition is raised. Each one of these specimens of gas was analysed by means of Hempel's apparatus modified for use on a small scale,* with interesting results. The actual volume of *nitrogen* in every grm. of material was found to be almost identical, diminishing only very slightly, if at all, as the temperature increased, and amounting to about 0·14 c.c. Thus the large differences in the total volumes are due almost wholly to *oxygen*, which varied from over 60 per cent in the first average to less than 20 per cent in the third. The small amount of carbon dioxide present was absorbed almost completely by the boiled water over which the gases were collected; hence it need not be considered.† The actual volumes of nitrogen in the five averages were respectively 0·138, 0·133, 0·130, in the first series, and 0·152 and 0·127 in the second series; while the actual amounts of oxygen were respectively 0·235, 0·087, 0·030, in the first series, and 0·191 and 0·065 in the second. No better proof could be desired of the fact that zincic oxide allows its oxygen to depart more easily than its nitrogen. These results are wholly confirmatory of the results of Richards and Rogers already mentioned; but of course they do not explain how Morse and Arbuckle, working at nearly constant temperature, obtained inconstant results. To accomplish this explanation, the other possible causes affecting the retention of gases must be considered.

The Effect of Time of Ignition on the Amount of Gas retained by Zincic Oxide.

First Series: Just above the Melting-point of Thallous Sulphate.

		C.c. gas.
44.	1 grm. of ZnO, heated at 660° for 1 hour, gave	0·46
34.	1 grm. of ZnO, heated at 660° for 3 hours, gave	0·36
35.	" " "	0·38
	Average	0·37

Second Series: Just above the Melting-point of Potassic Chloride.

45.	1 grm. of ZnO, heated at 750° for 10 mins., gave	0·27
46.	1 grm. of ZnO, heated at 750° for 20 mins., gave	0·35
40.	1 grm. of ZnO, heated at 750°, for 30 mins., gave	0·37
41.	" " "	0·32
	Average	0·35
47.	1 grm. of ZnO, heated at 750° for 60 mins., gave	0·30
48.	" " "	0·32
	Average	0·31
36.	1 grm. of ZnO, heated at 750° for 180 mins. gave	0·21
37.	" " "	0·25
		0·23

Third Series: Just above the Melting-point of Sodic Sulphate.

49.	1 grm. of ZnO, heated at 880° for 3 mins., gave	0·49
50.	1 grm. of ZnO, heated at 880° for 5 mins., gave	0·35
51.	1 grm. of ZnO, heated at 880° for 12 mins., gave	0·29
52.	" " "	0·25
	Average	0·27
42.	1 grm. of ZnO, heated at 880 for 30 mins., gave	0·19
43.	" " "	0·19
	Average	0·19
38.	1 grm. of ZnO, heated at 880° for 180 mins., gave	0·14
39.	" " "	0·18
	Average	0·16

In each of the series the same fact may be noted,—the fact that continued heating at any one temperature is capable of causing a slow evolution of gas from the oxide. Only in the second of these series is evident an initial increase in the amount of gas, indicating a maximum after less than twenty minutes of heating. This increase, which is manifestly due to the advancing decomposition of the traces of imprisoned nitrate, undoubtedly ceases after an hour's heating at 660°, or after three minutes' heating at 880°; hence it does not appear in the first and third series.

Fig. 2.

The steady loss of gas after this maximum has been attained—a loss increasing with time as well as with increasing temperature in the case of *zincic* oxide—is worthy of further attention, especially because it will be remembered that the amount of gas retained by *cupric* oxide remained almost constant until a very high temperature was reached. Analysis of the several specimens of gas showed at once wherein lay the explanation; for they showed as before that the maximal quantities of gas consisted chiefly of oxygen, while the gas obtained by the last two experiments consisted chiefly of nitrogen. Here again the nitrogen remained nearly constant, only diminishing from 0·20 c.c. at the maxima to about 0·13 c.c. at the minima; while the oxygen diminished in the same samples from 0·21 c.c. to 0·03 c.c.

(To be continued).

* The most important modification was the arrangement for connecting pipette to burette. By blowing and drawing down the capillary it may be made to fit so perfectly into the fine rubber tube as to make the loss of small bubbles impossible. The diagram will make the idea clear. (Fig. 2.)

† *Proceedings of the American Academy*, xxviii., 205, 209. In a number of cases where pains was taken to measure the carbon dioxide, its volume never exceeded 3 or 4 per cent, and was usually about 2 per cent.

CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.*

By A. B. PRESCOTT and H. M. GORDIN.

(Continued from p. 19).

Other Atropine Periodides, and Atropine Mercuric Iodides.

Having obtained the enneaiodide of atropine, it was natural to suppose the existence of a heptaiodide, with probability of a complete series from the tri-iodide to the enneaiodide. And in fact in the course of our work we once obtained this heptaiodide. But our efforts to determine the exact conditions necessary for the formation of this body have so far not been successful. Whether additional quantities of atropine will make the precipitate take up more atropine and become a lower periodide we shall try to determine by later experiments. On the other hand, when the order is reversed, and the iodine solution

* The portion of this article which concerns atropine was given in substance in the *Journ. Am. Chem. Soc.*, xx., 329, under the title, "Atropine Periodides and Iodomercurates," by H. M. Gordin and A. B. Prescott (reprints). Also that concerning morphine and opium, except the "Results of Opium Assay," appeared in Kremers' *Pharmaceutical Archives*, June, 1898, i., 121, under the title, "A Volumetric Assay of Opium," by H. M. Gordin and A. B. Prescott (reprints).

is added to the atropine solution, it is always a lower periodide that is formed; but whether on continued addition of the iodine the precipitate will take up more of it and become a higher periodide we cannot say as yet.

The easiest way to obtain the periodides of atropine is to use chloroform as a solvent. On adding 20 grms. atropine to a warm solution of 30 grms. iodine in chloroform (500 c.c.), the enneaiodide crystallises out very soon in the shape of small, shining, dark green crystals. If these be removed by filtration, the mother-liquor will give several successive crops of the dark blue pentaiodide, and at last a crop of the brownish-red tri-iodide.

Atropine mercuric iodides are best known as products of precipitation of atropine salts by Mayer's reagent, the solution of potassium mercuric iodide (Groves, 1859, *Quar. J. Chem. Soc.*, xi., 97, 188; F. F. Mayer, 1862, *Am. J. Pharm.*, xxxv., 20; Chemical News, vii., 159; viii., 177, 189; Prescott, 1880, *Am. Chem. J.*, ii., 294; xiv., 606). We find that they can be obtained by shaking the alcoholic solution of a periodide with metallic mercury and warming the mixture. Double iodides of atropine and mercury can also be made by mixing theoretical quantities of atropine and iodine, adding a little alcohol and an excess of mercury, slightly warming, and shaking till the colour of iodine disappears. If the higher periodides of atropine be used in the preparation of this double iodide of atropine and mercury, there is always separation of mercurous iodide; but if theoretical quantities of atropine and iodine be used there is no separation of mercurous iodide. The formula of this double iodide of mercury and atropine, as shown by our analysis, seems to be $C_{17}H_{23}NO_3{\cdot}HI{\cdot}HgI_2$. It resembles, in composition, several other double iodides of alkaloids and mercury obtained by Groves by a different method, and agrees in proportion with the strychnine compound, not with the morphine or quinine compound obtained by one of us in 1880 (Prescott, *Am. Chem. J.*, ii., 297). But besides this double iodide we also obtained another having the composition $(Atrop.\ HI)_2{\cdot}HgI_2$. It was made by treating a solution of the $(Atrop.\ HI){\cdot}HgI_2$ in diluted alcohol with an excess of potassium iodide. From the liquid obtained by shaking an alcoholic solution of atropine and iodine with mercury, the monoatropine hydriodide mercuric iodide crystallises out in shining, yellow crystals, melting at 80° to 90° C., difficultly soluble in ether or chloroform, partly soluble in hot water, and very soluble in warm alcohol. The diatropine hydriodide mercuric iodide obtained, as said above, by the action of potassium iodide on the mono compound, crystallises in perfectly white, silky needles, which, on being dried, assume a yellowish tint. They melt at 98° to 99° C., are very easily soluble in warm alcohol, and quite soluble in hot water.

The analysis for mercury and for iodine in these bodies can be made in different ways, but the best results are obtained by a modification of the method of Risse (*Ann. Chem., Liebig*, cvii., 223). The mercury and the iodine are determined in two separate portions. For mercury the substance is dissolved in a little warm alcohol and a little water added; the solution is then acidulated with a few drops of dilute hydrochloric acid, and saturated with hydrogen sulphide. The mercuric sulphide is then dried and weighed in the usual way. For the determination of iodine the substance is treated with a hot solution of potassium hydroxide (1 : 10), diluted with water, filtered, and when completely cold neutralised with acetic acid. The iodine is now precipitated with silver nitrate and nitric acid, and determined as silver iodide in the usual way.

In the following analyses the standard silver nitrate solution was made to correspond with 1 per cent of iodine, and the ammonium thiocyanate solution to correspond, c.c. per c.c., with the silver nitrate solution. The standard solution of iodine contained 1 per cent of iodine, and the sodium thiosulphate solution corresponded, c.c. per c.c., with the iodine solution.

Analyses of the Double Salts of Atropine Hydriodide and Mercuric Iodide.—0·2632 grm. of the monoatropine hydriodide mercuric iodide gave 0·0699 grm. mercuric sulphide, and 0·30445 grm. of the substance gave 0·24785 grm. silver iodide.

	Calculated for $C_{17}H_{23}NO_3{\cdot}HI{\cdot}HgI_2$.	Found.
Mercury	23·03	22·89
Iodine	43·74	43·98

Of the diatropine hydriodide mercuric iodide, 0·1798 grm. gave 0·032 grm. mercuric sulphide, and 0·257 grm. of the substance gave 0·18885 grm. silver iodide.

	Calculated for $(C_{17}H_{23}NO_3{\cdot}HI)_2HgI_2$.	Found.
Mercury	15·58	15·34
Iodine	39·46	39·70

Strychnine Heptaiodide and its Analysis.

The heptaiodide of strychnine is a dark brown powder, hardly soluble in ether, chloroform, or benzol, and requires considerable alcohol for solution. It cannot be re-crystallised, as it is easily decomposed into free iodine and the tri-iodide (a tri-iodide was reported by Tilden in 1865; see Geuther's lists, *loc. cit.*).

The total iodine was determined by silver nitrate after reduction with zinc and ammonia. The additive iodine was estimated after dissolving the periodide in alcohol by titrating with thiosulphate.

For total iodine:—

1. 0·3816 grm. of the periodide gave 0·51345 grm. silver iodide.
2. 0·30625 grm. gave 0·4112 grm. silver iodide.

	Calculated for $C_{21}H_{22}N_2O_2HI{\cdot}I_6$.	Found.
1	72·66	72·70
2	—	72·54

For additive iodine:—

1. 0·1754 grm. of the substance was found to contain 0·109 grm. free iodine.
2. 0·17805 grm. contained 0·111 grm. free iodine.

	Calculated for $C_{21}H_{22}N_2O_2{\cdot}HI{\cdot}I_6$.	Found.
1	62·28	62·14
2	—	62·34

Six atoms iodine coming from the free iodine of the iodopotassium iodide solution, we get the ratio, I_6 to $C_{21}H_{22}N_2O_2$, or 1 of iodine to 0·439 of strychnine absolute. This gives the *decinormal factor* (the value of 1 c.c. of decinormal iodine solution) as 0·0055547 for strychnine.

Brucine Heptaiodide and its Analysis.

This was made according to the general method already given, by pouring a ½ per cent solution of brucine acidulated with hydrochloric acid into a large excess of a 1 per cent solution of iodine. In appearance and solubility it closely resembles the heptaiodide of strychnine, but it exercises a strong reducing action on silver salts, so that its analysis for total iodine is best accomplished by the aid of nitrous acid and bisulphide of carbon as described under the head of morphine tetraiodide and its analysis.

For total iodine:—

1. 0·1916 grm. of the periodide was found to contain 0·13229 grm. total iodine.
2. 0·2395 grm. of the periodide contained 0·16536 grm. total iodine.

	Calculated for $C_{23}H_{26}N_2O_4{\cdot}HI{\cdot}I_6$.	Found.
1	69·21	69·04
2	—	69·04

For additive iodine:—

1. 0·1622 grm. of the substance contained 0·096006 grm. free iodine.
2. 0·192 grm. contained 0·114 grm. free iodine.

	Calculated for $C_{23}H_{26}N_2O_4 \cdot HI \cdot I_6$.	Found.
1	59·32	59·19
2	—	59·37

For brucine, therefore, the ratio is I_6 to $C_{23}H_{26}N_2O_4$, or 1 of iodine to 0·5179 of anhydrous brucine. And 1 c.c. of strictly decinormal solution of iodine indicates 0·0065530 of brucine, *the decinormal factor*, subjected to trial as stated later.

Morphine Tetraiodide and its Analysis.

Two samples were made. In the first, 1 grm. of morphine dissolved in 200 c.c. acidulated water was added to a solution of 5 grms. iodine and 7½ grms. potassium iodide in 500 c.c. water, the mixture shaken till the supernatant liquid was perfectly clear, and the precipitate washed and dried in vacuum. In the second, 2 grms. iodine and 3 grms. potassium iodide were dissolved in 200 c.c. water, and the solution poured slowly into a solution of morphine containing 3 grms. morphine in 600 c.c. acidulated water. The analysis, as given below, showed that the precipitate in both cases was the same, namely, $C_{17}H_{19}NO_3HI \cdot I_3$. This compound, morphine tetraiodide, was made known by Jörgensen in 1870 (*J. Prakt. Chem.* (2), ii., 437). We find it to be the only periodide formed by morphine under any of the conditions of this precipitation from aqueous solutions.* It is notable that in this periodide the base as a monamine holds an even number of atoms of total iodine. The periodide precipitate of morphine is practically insoluble when the iodine is in excess, though appreciably soluble when the morphine is in excess, as it is in pure water, the more so if strongly acidulated.

In the analysis of the morphine periodide, the precipitate is to be collected and quickly washed with water by the aid of the pump, and then dried in vacuum over sulphuric acid to a constant weight. The additive iodine is readily determined, in a weighed portion, by dissolving in alcohol and titrating with a standard solution of sodium thiosulphate, as stated in previous paragraphs. The total iodine determination in this compound gives special difficulty, as neither the sulphur dioxide nor the powdered zinc, previously used in this laboratory for analytical reduction of periodides, works well with morphine periodide, but the following procedure suffices. The periodide is covered with powdered zinc and stronger water of ammonia and set aside half an hour, the mixture is then heated on the water-bath till all the ammonia is driven off, avoiding loss by spurting. A little water is now added and the mixture boiled about ten minutes. The whole is filtered into a separator of about 500 c.c. capacity, the excess of zinc well washed with hot water, and water added to make 200 or 300 c.c. When perfectly cold the mixture is acidified slightly with very dilute sulphuric acid, then 20 c.c. of carbon disulphide are poured into the separator, and 10 to 12 drops of concentrated sulphuric acid *saturated with nitrous acid* are added. The separator is closed and shaken, and the solution of iodine in carbon disulphide carefully run out upon a wetted filter. Fresh carbon disulphide is added in the separator, and the separation repeated till all the iodine is removed. The iodine is now washed on the filter, first with water, then with a very weak solution of sodium bicarbonate. It is then run into a flask, and 30 c.c. of a solution of sodium bicarbonate, 5 grms. to the litre, are added. Finally the iodine is titrated with the standard solution of sodium thiosulphate. The results were as follows:—

I. Iodine in excess:—

0·2692 grm. gave 0·13 grm. additive iodine, and 0·2732 grm. gave 0·174311 grm. total iodine.

	Calculated for $C_{17}H_{19}NO_3 \cdot HI \cdot I_3$.	Found.
Additive iodine..	48·02	48·29
Total iodine	64·03	63·80

II. Morphine in excess:—

0·3155 grm. were found to contain 0·152832 grm. additive iodine, and 0·2708 grm. contained 0·172076 grm. total iodine.

	Calculated for $C_{17}H_{19}NO_3 \cdot HI \cdot I_3$.	Found.
Additive iodine..	48·02	48·44
Total iodine	64·03	63·54

For morphine the ratio is I_3 to $C_{17}H_{19}NO_3$, or ratio of 379·59 to 284·38, that is 1 of free iodine consumed to 0·74918 of morphine, anhydrous. And 1 c.c. of strictly decinormal solution of iodine corresponds to 0·0094794 grm. of morphine.

Aconitine Heptaiodide (?) and its Analysis.

The alkaloid we used was obtained from Merck, and marked "From Acontum Napellus, crystallised, pure." This periodide was made according to the general plan of obtaining the highest periodide of an alkaloid.

For additive iodine 0·2588 grm. contained 0·126886 grm. free iodine, and 0·1471 grm. contained (by nitrous acid method) 0·082271 grm. total iodine.

	Calculated for $C_{33}H_{45}NO_{12} \cdot HI \cdot I_6$.	Found.
Additive	49·58	49·03
Total	57·85	55·93

We make our calculations upon the aconitine formula of Dunstan (*J. Chem. Soc.*, lxvii., 459). The formula of Freund (*Ber. d. Chem. Ges.*, xxvii., 722), though distinctly different in constitution, gives but slightly different molecular weight. Other proposed formulæ approach the same molecular weight. $C_{34}H_{47}NO_{11} = 643·55$ (Freund). $C_{33}H_{45}NO_{12} = 645·54$ (Dunstan). $C_{33}H_{47}NO_{12} = 647·54$ (Jürgens). $C_{33}H_{43}NO_{12} = 643·54$ (Wright and Luff).

An insufficiency of the aconitine in our hands prevented our making duplicate estimations. With both the higher and the lower periodide, it is to be seen that the total iodine found is somewhat too low for the calculated quantity of this element, calculating for heptaiodide and tri-iodide respectively. The additive iodine in both cases falls below calculation, but not enough below to discredit the formulæ. When we return to these estimations with a larger supply of the alkaloid, we shall find whether the instability of aconitine will prevent constant results in analysis of the higher periodide or not.

Aconitine Tri-iodide (?).

This was made by adding a 1 per cent solution of iodine to an acidulated solution of aconitine, leaving the latter in excess, and re-crystallising the precipitate from alcohol. Thus obtained it forms beautiful brown-red crystals, very soluble in alcohol, insoluble in water, and hardly soluble in ether, benzol, or chloroform. Melting-point, 211—212° C.

For additive iodine:—

0·01773 grm. of the substance contained 0·042352 grm. free iodine.

Calculated for $C_{33}H_{45}NO_{12} \cdot HI \cdot I_2$.	Found.
24·69	23·89

For total iodine by the aid of nitrous acid and bisulphide of carbon, as given under the head of morphine.

0·2111 grm. contained 0·07505 grm. total iodine.

Calculated for $C_{33}H_{45}NO_{12} \cdot HI \cdot I_2$.	Found.
37·03	35·56

(To be continued).

* The present hypothesis of structure of periodides would imply, therefore, that the compound is a dimorphine octaiodide (*Journ. Am. Chem. Soc.*, xvii., 780; xix., 331). A lower periodide of morphine was obtained by evaporation of an alcoholic solution containing excess of morphine, by H. R. Bauer (*Arch. Pharm.* [3], v., 289-309).

DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.*

By J. MERRITT MATTHEWS.

(Continued from p. 17).

D. *Propylamine.*

a. Zirconium Tetrachloride, $ZrCl_4.4C_3H_7NH_2$. — With propylamine, zirconium tetrachloride gave a white compound similar in appearance to the foregoing derivatives.

0·3390 grm. material gave :—
0·4112 grm. silver chloride = 0·1020 grm. chlorine = 30·10 per cent chlorine.
0·0897 grm. zirconium dioxide = 0·0663 grm. zirconium = 19·55 per cent zirconium.

0·6229 grm. material gave :—
0·0892 grm. ammonia = 0·0736 grm. nitrogen = 11·80 per cent nitrogen.

	Calculated for $ZrCl_4.4C_3H_7NH_2$.	Found.
Chlorine	30·30	30·10
Zirconium	19·33	19·55
Nitrogen	11·96	11 80

b. Thorium Tetrachloride, $ThCl_4.4C_3H_7NH_2$.—Propylamine gave a white compound with thorium tetrachloride.

0·2682 grm. material gave :—
0·2537 grm. silver chloride = 0·0628 grm. chlorine = 23·40 per cent chlorine.
0·1167 grm. thorium dioxide = 0·1026 grm. thorium = 38·22 per cent thorium.

0·4213 grm. material gave :—
0·0460 grm. ammonia = 0·0379 grm. nitrogen = 9·01 per cent nitrogen.

	Calculated for $ThCl_4.4C_3H_7NH_2$.	Found.
Chlorine	23·25	23·40
Thorium	38·09	38·22
Nitrogen	9·18	9·01

c. Lead Tetrachloride, $PbCl_4.4C_3H_7NH_2$. — Propylamine at first gave a dark reddish brown precipitate with lead tetrachloride, soon becoming almost white in colour, having a faint yellow tinge.

0·2507 grm. material gave :—
0·2065 grm. silver chloride = 0·0511 grm. chlorine = 20·39 per cent chlorine.
0·2672 grm. material gave :—
0·1195 grm. lead sulphate = 0·0817 grm. lead = 30·56 per cent lead.

0·2817 grm. material gave :—
0·1513 grm. platinum = 0·0217 grm. nitrogen = 7·82 per cent nitrogen.

	Calculated for $PbCl_4.4C_3H_7NH_2$.	Found.
Chlorine	20·73	20·39
Lead	30·22	30·56
Nitrogen	8·28	7·82

E. *Aniline.*

Schiff (*Jahresb. Chem.*, 1863, 412) has obtained a compound of tin tetrachloride with aniline, to which he has given the formula $SnCl_4.4C_6H_5NH_2$; while with titanium tetrachloride Leeds (*Journ. Am. Chem. Soc.*, iii., 145) describes a derivative having the formula $TiCl_4.4C_6H_5NH_2$.

In all of these derivatives the aniline appears to be merely additive. With silicon tetrachloride, however, aniline seems to form a substitution product corresponding to the formula $SiCl_2.(C_6H_5NH)_2$ (Harden, *Journ. Chem. Soc.*, li., 40; Reynolds, *Ibid.*, lv., 474; and Harold, "Thesis," Univ. of Pennsylvania, 1897).

a. Zirconium Tetrachloride, $ZrCl_4.4C_6H_5NH_2$.—On the addition of aniline to the solution of zirconium tetrachloride a greyish flocculent precipitate was produced. This was carefully washed with anhydrous ether until all traces of aniline were removed. It appeared to be stable on drying, and its analysis showed the presence of four molecules of aniline.

I. 0·5382 grm. material gave :—
0·5053 grm. silver chloride = 0·1251 grm. chlorine = 23·25 per cent chlorine.
0·1080 grm. zirconium dioxide = 0·0798 grm. zirconium = 14·83 per cent zirconium.

II. 0·4817 grm. material gave :—
0·4538 grm. silver chloride = 0·1123 grm. chlorine = 23·32 per cent chlorine.
0·0982 grm. zirconium dioxide = 0·0726 grm. zirconium = 15·06 per cent zirconium.

I. 0·5382 grm. material gave :—
0·0600 grm. ammonia = 0·0494 grm. nitrogen = 9·19 per cent nitrogen.

II. 0·6108 grm. material gave :—
0·0678 grm. ammonia = 0·0559 grm. nitrogen = 9·15 per cent nitrogen.

	Calculated for $ZrCl_4.4C_6H_5NH_2$.	Found. I.	Found. II.
Chlorine	23·49	23·25	23·32
Zirconium	14·98	14·83	15·06
Nitrogen	9·27	9·19	9·15

Since analysis would show no difference in the composition of $ZrCl_4.4C_6H_5NH_2$ and a mixture of $ZrCl_2(C_6H_5NH)_2 + 2C_6H_5NH_2.HCl$, the following method was resorted to in order to prove that it was the first and not the second compound which was formed. The substance, after having been completely freed from aniline, was treated with chloroform, in which it proved to be easily and completely soluble, whereas aniline hydrochloride is insoluble in the same reagent, and hence was not present in the compound. Also no substituted chloraniline, $C_6H_4ClNH_2$, could have been formed, as this is soluble in ether, and the existence of no such substance was indicated in the ethereal filtrate. This conclusively proves that the compound is purely additive in nature, and has the formula $ZrCl_4.4C_6H_5NH_2$. This same proof may be used as an argument for the additive character of all the zirconium and thorium derivatives described in this research.

b. Thorium Tetrachloride, $ThCl_4.4C_6H_5NH_2$.—Aniline produced a precipitate slightly grey in colour, and soluble in chloroform. Its analysis indicated a formula in correspondence with that of the zirconium derivative.

0·2536 grm. material gave :—
0·1940 grm. silver chloride = 0·0479 grm. chlorine = 18·89 per cent chlorine.
0·0906 grm. thorium dioxide = 0·0796 grm. thorium = 31·39 per cent thorium.

0·5536 grm. material gave :—
0·0488 grm. ammonia = 0·0402 grm. nitrogen = 7·41 per cent nitrogen.

	Calculated for $ThCl_4.4C_6H_5NH_2$.	Found.
Chlorine	19·02	18·89
Thorium	31·15	31·39
Nitrogen	7·61	7·41

c. Lead Tetrachloride, $PbCl_4.3C_6H_5NH_2$.—Aniline gave a dark green stable compound with lead tetrachloride in dilute solution. A more concentrated solution of the lead salt reacts very violently with aniline, probably giving rise to the same chlorinated products as tin tetrachloride, such as violaniline, mauvaniline, rosaniline, and triphenylendiamine blue (Girard and Pabst, *Bull. Soc. Chim.*, xxxiv., 33). The dark green compound analysed for three molecules of aniline.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx., No. 11. From author's thesis for the Degree of Doctor of Philosophy.

0·2104 grm. material gave:—
0·1950 grm. silver chloride = 0·0483 grm. chlorine = 22·94 per cent chlorine.
0·2042 grm. material gave:—
0·0963 grm. lead sulphate = 0·0658 grm. lead = 32·22 per cent lead.
0·4012 grm. material gave:—
0·1929 grm. platinum = 0·0277 grm. nitrogen = 6·90 per cent nitrogen.

	Calculated for $PbCl_4 \cdot 3C_6H_8NH_2$.	Found.
Chlorine	22·61	22·94
Lead	32·96	32·22
Nitrogen	6·69	6·90

F. *Toluidine.*

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 4C_6H_4CH_3NH_2$.—As aniline gave a derivative with zirconium tetrachloride, toluidine was also tried with like result. Analysis indicated that this compound contained four molecules of toluidine, showing it to be analogous to the aniline derivative.

0·3772 grm. material gave:—
0·3240 grm. silver chloride = 0·0802 grm. chlorine = 21·26 per cent chlorine.
0·0694 grm. zirconium dioxide = 0·0512 grm. zirconium = 13·60 per cent zirconium.
0·4296 grm. material gave:—
0·0456 grm. ammonia = 0·0376 grm. nitrogen = 8 74 per cent nitrogen.

	Calculated for $ZrCl_4 \cdot 4C_6H_4CH_3NH_2$.	Found.
Chlorine	21·50	21·26
Zirconium	13·72	13·60
Nitrogen	8·48	8·74

b. Thorium Tetrachloride, $ThCl_4 \cdot 3C_6H_4CH_3NH_2$.—This was a greenish white precipitate and showed a departure from the other derivatives and from its analogous zirconium compound in that it only contained three molecules of the base.

0·5012 grm. material gave:—
0·4074 grm. silver chloride = 0·1008 grm. chlorine = 20·12 per cent chlorine.
0·1940 grm. thorium dioxide = 0·1705 grm. thorium = 34·01 per cent thorium.
0·7500 grm. material gave:—
0·0526 grm. ammonia = 0·0433 grm. nitrogen = 5·78 per cent nitrogen.

	Calculated for $ThCl_4 \cdot 3C_6H_4CH_8NH_2$.	Found.
Chlorine	20·41	20·12
Thorium	33·44	34·01
Nitrogen	6·04	5·78

c. Lead Tetrachloride.—With toluidine no additive product could be obtained even by using quite dilute solutions of lead tetrachloride, as the amine was decomposed, giving a deep purple solution. Hence lead tetrachloride evidently has about the same action on toluidine as bleaching lime or tin tetrachloride.

G. *Pyridine.*

As pyridine and quinoline are strong bases, and as they may be considered tertiary amines, it was thought probable that these reagents would form derivatives with the tetrachlorides in a manner similar to aniline and toluidine. Experiment proved this surmise to be a correct one, as a compound was formed in both instances. It may be stated that Classen and Zahorski (*Zeit. Anorg. Chem.*, iv., 100) have obtained compounds of lead tetrachloride with the hydrochlorides of pyridine and quinoline, and they are described as additive products. Goebbles (*Ber. d. Chem. Ges.*, xxviii., 792) has also obtained compounds of lead tetrachloride with the salts of such complex organic bases as picoline, lutidine, and collidine.

The compounds of zirconium and thorium tetrachlorides with pyridine and quinoline are light grey to brown flocculent precipitates. Unlike the derivatives with the preceding amines, they appeared to be rather unstable in moist air, in consequence of which considerable difficulty was experienced in obtaining suitable portions for analysis, as the compounds had to be preserved under anhydrous ether.

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 2C_5H_5N$.—The best analysis that could be obtained for the pyridine derivative approximated to a formula containing two molecules of the base.

0·5420 grm. material gave:—
0·7805 grm. silver chloride = 0·1932 grm. chlorine = 35·64 per cent chlorine.
0·1758 grm. zirconium dioxide = 0·1299 grm. zirconium = 23·97 per cent zirconium.
0·6118 grm. material gave:—
0·0506 grm. ammonia = 0·0417 grm. nitrogen = 6·83 per cent nitrogen.

	Calculated for $ZrCl_4 \cdot 2C_5H_5N$.	Found.
Chlorine	36·35	35·64
Zirconium	23·19	23·97
Nitrogen	7·18	6·83

b. Thorium Tetrachloride, $ThCl_4 \cdot C_5H_5N$.—0·5002 grm. material gave:—
0·6270 grm. silver chloride = 0·1552 grm. chlorine = 31·02 per cent chlorine.
0·2939 grm. thorium dioxide = 0·2583 grm. thorium = 51·64 per cent thorium.
0·4107 grm. material gave:—
0·0126 grm. ammonia = 0·0104 grm. nitrogen = 2·53 per cent nitrogen.

	Calculated for $ThCl_4 \cdot C_5H_5N$.	Found.
Chlorine	31·30	31·02
Thorium	51·28	51·64
Nitrogen	3·09	2·53

c. Lead Tetrachloride, $PbCl_4 \cdot 2C_5H_5N$.—Pyridine gave a pale yellow precipitate with lead tetrachloride of much greater stability than the foregoing compounds.
0·2506 grm. material gave:—
0·2780 grm. silver chloride = 0·0688 grm. chlorine = 27·46 per cent chlorine.
0·3125 grm. material gave:—
0·1842 grm. lead sulphate = 0·1258 grm. lead = 40·26 per cent lead.
0·3062 grm. material gave:—
0·1112 grm. platinum = 0·0161 grm. nitrogen = 5·21 per cent nitrogen.

	Calculated for $PbCl_4 \cdot 2C_5H_5N$.	Found.
Chlorine	28·01	27·46
Lead	40·83	40·26
Nitrogen	5·52	5·21

(To be continued).

Messrs. John J. Griffin and Sons, Ltd., the well-known makers of scientific instruments, who have removed from their old premises in Garrick Street to Sardinia Street, Lincoln's Inn Fields, have sent us their Catalogue —Part III., Magnetism, Electricity, and Galvanism. The list includes some of the latest pieces of apparatus, as well as some almost obsolete. We note several forms of Wimshurst electrical machines, Kelvin's galvanometers, Ayrton weather instruments, Röntgen ray outfits, telephones, arc lamps, and electric furnaces. The illustrations are good and numerous, and the catalogue is likely to prove of great use to any having the responsibility of schools and technical institutions, especially those in country places.

NOTICES OF BOOKS.

A Manual of Chemical Analysis, Qualitative and Quantitative. By G. S. Newth, F.I.C., F.C.S. London, New York, and Bombay: Longmans, Green, and Co. 1898. Pp. 462.

The volume now before us treats the subject of both qualitative and quantitative analysis in a clear and comprehensive manner. Beginning with the simplest reactions in both the wet and dry ways, the student is led on through simple tests to group analysis, after which the rare earths and metals are dealt with. When this branch has been thoroughly mastered, the principles and practice of quantitative analysis are fully explained, both gravimetrically and volumetrically. A very good plan has been adopted in first giving an "epitome of process," and then proceeding to the more detailed instructions for carrying out whatever analysis or process is being dealt with.

The book is very well adapted for both class and laboratory work, and should rank among the standard text-books of science.

Practical Pharmacy: an Account of the Methods of Manufacturing and Dispensing Pharmaceutical Preparations, with a Chapter on the Analysis of Urine. By E. W. Lucas, F.C.S. With 283 Illustrations. Pp. 528. London: J. and A. Churchill. 1898.

Although a certain portion of this work is devoted to manufacturing processes, the bulk of it deals with the ordinary method and routine of pharmacy and dispensing. It is essentially a book for students, beginning as it does with the simplest chemical instruction. There is, however, too great a tendency in such books now-a-days to assume that the reader or student knows nothing of the subject he is taking up as a profession; we very much doubt if the early chapters are ever read, filled as they are with descriptions and illustrations of the simplest and commonest articles used in chemical laboratories. Tables of weights and measures, and such like information, are supposed to be learnt at school, and a quarter-page illustration of copper gallon and quart measures surely seems unnecessary.

The book is divided into six parts, comprising general processes and descriptions of apparatus, pharmacopœial preparations, dispensing, pharmaceutical tests, volumetric and gravimetric analysis, tables, and a chapter on the analysis of urine, in which will be found a number of excellent enlarged microscopic plates.

After the preliminaries are got over the book will be found to be sound, and clearly written, and will be of value to the student. There is a copious index of eleven pages.

CORRESPONDENCE.

THE ORIGIN OF THE GASES EVOLVED ON HEATING MINERAL SUBSTANCES, METEORITES, &c.

To the Editor of the Chemical News.

Sir,—In an interesting paper on the above subject recently read before the Royal Society, and published in the Chemical News (lxxviii., p. 305), Dr. M. W. Travers discusses the source of the gases given off on heating meteorites. The conclusion he arrives at is thus stated in his own words:—"It would appear then that the gases produced by the action of heat upon meteorites are not present as such, but are the products of decomposition of their non-gaseous constituents. It is therefore impossible to draw conclusions as to the former history of a meteorite from the nature of ths gases which it gives on heating."

From the tenour of some of the remarks made by Dr Travers, I judge that he is not aware that the same conclusion has been reached before. May I therefore draw attention to a paper in the *Philosophical Magazine* of June, 1883, on the "Regenerative Theory of Solar Action"; where, in discussing the well-known speculation of the late Sir William Siemens, I have considered the question as to whether the composition of the gases found occluded in meteorites supports the view of the existence of an atmosphere rich, in hydrogen, existing in space. After quoting the experimental results, and explaining how the gases can be formed from the substances contained in the meteorites themselves, I conclude "that they afford us no insight into the composition of the supposed interplanetary atmosphere."—I am, &c.,

Ernest H. Cook.

The Clifton Laboratory,
January 10, 1899.

ESTIMATION OF LEAD.

To the Editor of the Chemical News.

Sir,—In reply to the second question of your querist "Cox" (Chem. News, lxxix., 12), may I say that the estimation of lead, outlined in the Appendix of Mr. Brearley's paper on the "Estimation of Molybdenum Compounds," could be readily adapted to the determination of lead in iron and calcium compounds. As it is very unlikely that any satisfactory precipitation of lead molybdate can be made in the presence of iron, that element would need to be separated. Either alkaline acetates or soda hydrate could, I believe, be used to this end.

The very large number of elements in whose presence molybdenum has been shown to be accurately precipitable as lead molybdate by a lead salt, at once suggests the converse operation of estimating lead in their presence. If in this converse operation there can be added tin, antimony, and bismuth to those elements Mr. Brearley has already experimented with, then the method would be a valuable one for the examination of the numerous commercial lead alloys.

This line of investigation I have been for some time engaged upon, and hope shortly to publish the results, amongst others, of special interest to "Cox."—I am, &c.,

R. Leffler.

The Laboratory,
Thos. Firth and Sons, Lim., Sheffield.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

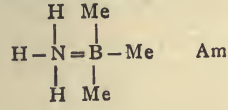
Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 21, November 21, 1898.

Relation between Luminous and Chemical Energy and Displacement of the Halogen Elements by Oxygen.—M. Berthelot.—The author examines—(1) The action of iodine and oxygen, finding that iodic anhydride and also iodic hydrate are slowly decomposed into their elements under the influence of solar light at ordinary temperatures, the effect of the light being the same as that of heat, if the temperature of the snbstance is raised in the absence of light. This action, however, is not reversible, iodine and oxygen not combining at any known temperature. This reaction proves, what the author has also studied experimentally, that solar light does not in any degree change ordinary oxygen into ozone. For, this being the case, iodine must be at once oxidised. The same experiments were repeated in the presence of water

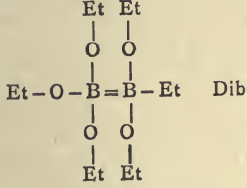
with again negative results. (2) The action of bromine and oxygen, finding that bromine or chlorine and free oxygen do not combine. However, chlorine and even bromine decompose water in the cold, giving off oxygen. The action of bromine on water is almost imperceptible in darkness, but quite perceptible under the influence of solar light. Reciprocally bromic acid is decomposed by oxygen at a high temperature.

Atomicity of Boron.—E. Frankland.—Referring to M. Copaux's paper on the new compound of boron which indicates its pentatomicity, the author states that in 1876 he obtained with boric methide and boric ethide a number of compounds, for which were suggested the formulæ—



Ammonia boric methide,

and—



Diboric altropentethylate,

&c.

which confirms the pentatomicity of boron and its power of uniting with itself in the same manner as carbon.

No. 22, November 28, 1898.

Condensed Oxides of the Rare Earths.—G. Wyrouboff and A. Verneuil.—The authors have examined the oxides of cerium with a view to replacing the confused notion of basic salts by the exact theory of successive condensation of the oxide. It appears much more rational to consider the combinations as neutral or acid salts of an oxide, which in condensing necessarily changes its valency. One of the most characteristic properties of the rare earths is their faculty of polymerising, under the influence of the most varied causes, and also their tendency to form among themselves very stable compounds of complex oxides, which properties naturally are expected from the above theory.

Observations on the Spectra of Aluminium, Tellurium, and Selenium.—A. de Gramont.—The author finds that certain lines in the spark spectrum of aluminium, tellurium, and selenium, as measured by Thalén and by himself in former papers, are due to impurities. He has obtained aluminium in a greater state of purity than that in which it has been obtained before, and from a study of the spectrum attributes Thalén's lines 637·13, 634·48, and 505·66, to silicon. In tellurium and selenium the lines 521·7, 515·3, 510·5 he attributes to copper.

Aromatic Urethanes of Tetrahydroquinoline.—MM. Cazeneuve and Moreau.—The action of secondary bases of the aromatic series on phenolic carbonates gives rise to urethanes, as shown by the derivatives of piperidine, conicine, piperazine, before described. The action of tetrahydroquinoline confirmed this reaction, which appears to be general for bodies of this type. An excess of base was used. On heating for two hours to the boiling-point 4 molecules of tetrahydroquinoline with 1 molecule of phenol carbonate, the following urethanes were obtained:—Phenyl, orthochlorphenyl, guaiacol, and α- and β-naphthol. These are all white bodies, very stable, fusible, and boiling almost without decomposition at about 300°.

Action of Potash on Oxynitrocellulose.—Léo Vignon.—Oxycellulose having been nitrated by a mixture of 1 part of H_2SO_4 and 3 parts of HNO_3, the oxynitrocellulose obtained was mixed with KOH, and the temperature raised to 45° for seven minutes. At the same time the oxynitrocellulose dissolved with a slight evolution of gas giving a brown liquid. This solution was cooled to 0°, and neutralised by acetic acid; it then became nearly colourless, and on a current of H_2S being passed through at the ordinary temperature, oxides of nitrogen were evolved, sulphur deposited, and a brown liquid obtained. This liquid, to which was added a solution of acetic acid and phenyl-hydrazine, was warmed to 80°, resulting in the formation of a crystalline precipitate: 100 grms. of oxynitrocellulose yielded 8 grms. of this precipitate, which consists of small yellow crystals. Analysis gave the following percentages:—C 64·40, N 19·33, H 5·40, O 11·87. The melting-point, 204, is identical with that of the osazone of oxypyruvic acid, and the analysis gives the same composition. Hence oxypyruvic acid,—

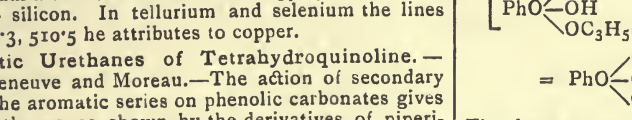
$$OH.CH_2CO.CO.OH = C_3H_4O_4$$

is the result of treating oxynitrocellulose with potash.

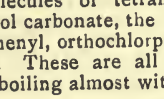
Journal de Pharmacie et de Chimie, vol. viii., No. 4.

Researches on Urinary Phosphorus.—L. Jolly.—These researches show that the urinary phosphorus which escapes estimation by the ordinary methods used for phosphoric acid is not incompletely oxidised phosphorus, or phosphoglyceric acid, according to one hypothesis which has been put forward, but simply phosphoric acid combined with metallic bases, again intimately associated with nitrogenous matter, an association which resists the action of digestives, and of the intra-organic oxidants.

The Organic Phosphoglycerates.—MM. Adrian and Trillat.—The preparation of the organic phosphoglycerates (of cocaine, quinine, phenyl-hydrazine, &c.) is as follows:—A solution of a neutral glycerophosphate of lime is treated with dilute sulphuric acid until it is just acid to heliantine, and is then brought back to neutrality with a few drops of neutral glycerophosphate; heat and filter off the calcic sulphate thus precipitated. After having added the base until the reaction is alkaline, and then a great excess of alcohol, the whole must be again heated for a few minutes, and filtered with a filter-pump to separate the precipitated glycerophosphate of lime; the solution must be concentrated at as low a temperature as possible, and desiccated *in vacuo* over sulphuric acid; the residue is taken up with a little water, and shaken up several times with ether, to remove all excess of the base; the aqueous solution is again evaporated down, and the residue triturated with strong alcohol. The unprecipitated phosphoglycerate of lime remains in suspension; the residue soluble in alcohol is finally dried at 50° to 60°. The strong bases only (quinine and cocaine) seem able to completely displace the lime of the acid phosphoglycerate according to the equation—



The less strong bases (aniline, phenyl-hydrazine, pyridine, &c.) precipitate a certain amount of the neutral phosphoglycerate of lime, but the residue from the filtrate contains a considerable proportion of a body either insoluble or only slightly soluble in alcohol: it has the formula—



The Decolouration of Wines by means of Salts of Manganese.—P. Jacob.—Not suitable for abstraction.

The Purification of Potable Waters.—P. Guichard.—The author points out that the water of the River Vanne contains 700 microbes per c.c. when it arrives in Paris, and that this number has increased to 212,000 by

the time it reaches the consumer. He therefore thinks that the purification of the water should be undertaken individually by the use of filters, the merits of some of which he discusses.

The Coagulation of Albumen.—G. Halphen.—From experiments made, and here described, the author concludes that some ammonium salts, such as the citrate and hydrochlorate, favour the separation of albumen; that the soda set free at the moment of coagulation displaces the alkali of the ammonia salt, thus creating a more favourable medium for coagulation; that the coagulation of albumèn is complete in the presence of citrate or of ammoniacal salts; and that operations carried out for the purpose of estimating the albumen are much more exact and are less troublesome when ammonia salts are used.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8 (Cantor Lectures). "Bacterial Purification of Sewage," by Dr. Samuel Rideal.
TUESDAY, 24th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.
—— Society of Arts, 4.30. "Rhodesia and its Mines in 1898," by W. Fischer Wilkinson, F.G.S.
WEDNESDAY, 25th.—Society of Arts, 8. "Tuberculosis in Animals," by W. Hunting.
THURSDAY, 26th.—Royal Institution, 3. "Tibet and the Tibetans," by A. Henry Savage Landor.
FRIDAY, 27th.—Royal Institution, 9. "Epitaphs," by Sir Mountstuart E. Grant Duff, F.R.S.
—— Physical, 5. "On the Equivalent Resistance and Inductance of a Wire to an Oscillatory Discharge," by E. H. Barton, D.Sc. Exhibition of (*a*) Dephlegmator, (*b*) A Temperature Tell-Tale, by R. Appleyard. "On the Volume Changes accompanying Solution," by T. H. Littlewood.
SATURDAY, 28th.—Royal Institution, 3. "Tschaikowsky" (with Musical Illustrations), by Sir Alexander C. Mackenzie, Mus. Doc.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2044.

THE PREPARATION AND SOME OF THE PROPERTIES OF PURE ARGON.*

By WILLIAM RAMSAY, F.R.S., and MORRIS W. TRAVERS.

IN the memoir on argon, and new constituent of the atmosphere (*Phil. Trans.*, A, Part I., 1895, p. 187), by Lord Rayleigh and one of us, reasons are adduced on pages 235 and 236 in favour of the supposition that argon is an element, or a mixture of elements; and on page 236 the following words occur:—"There is evidence both for and against the hypothesis that argon is a mixture, for, owing to Mr. Crookes's observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture." And on pages 257-259 of the same volume, it is shown by Professor Sydney Young and one of us that the ratios between the boiling-points of argon and benzene, argon and alcohol, and argon and oxygen on the absolute scale are such that it is possible to compute the boiling-points of argon at different pressures with very considerable accuracy. We therefore draw the conclusion:—"It is hardly likely, though not impossible, that so good an agreement would be obtained with a mixture or an impure substance. It is, at any rate, certain that a distinct want of agreement would have shown that argon was not a definite, pure substance, and the results may be taken as affording additional confirmation of the conclusion that argon is a definite, hitherto unknown constituent of the atmosphere, and that it has been isolated in a state very closely approaching to purity."

The density of a sample of argon prepared by means of magnesium was found by one of us to be 19·941 (O=16); and a much larger preparation by Lord Rayleigh, obtained by exposing a mixture of air and oxygen to an electric flame in presence of caustic soda, possessed the density 19·94. Supposing argon to be a simple substance, and not a mixture, the atomic weight would therefore be 39·88. An attempt was made by Dr. J. Norman Collie and one of us to effect a separation of argon into a light and a heavy portion passing by diffusion, but without definite results. While the density of the portion passing first through the pipe-clay septum was 19·93, that of the last portions was 20·01. We remarked on these figures in the following terms:—"These numbers show that no important separation has been effected. The difference in density of the two portions may possibly be attributed to experimental error. . . . As it stands, the difference is an extremely minute one, and it may, we think, be taken that any separation of argon, if effected at all, is very imperfect."

It thus remained uncertain whether argon was a mixture or not, although the balance of evidence went against the supposition.

When helium was discovered in 1895 a new light was thrown on the question. Its density, determined by Ramsay, and independently by Langlet, closely approximates to 2·0. Experiments, in conjunction with Dr Collie, and subsequently by ourselves, showed that no great difference in density could be brought about by fractional diffusion, and, indeed, the latter revealed no impurity, except traces of argon. On grounds similar to those from which a corresponding conclusion for argon was drawn, the atomic weight of helium must be somewhat below 4·0. The difference between the atomic weights of helium and argon is consequently about 36; and this is approximately the difference between the atomic weights of manganese and fluorine (36), chromium and oxygen (36·3), vanadium and nitrogen (37·4), and titanium and carbon (36·4). But between each of these pairs of elements there exists another, exceeding in atomic weight the lower member of each pair by approximately 16. It was therefore to be expected that another element should exist with atomic weight about 20, and on the assumption that, like helium and argon, it too would be a monatomic gas, its density would be 10. It was with the object of attempting to discover this unknown gas that the experiments on the fractional diffusion of helium were made, and the gases evolved on heating some fifty minerals were investigated in order to find out whether a new spectrum could be observed, but with negative results. Seven meteorites were also examined, as well as six mineral waters, but no new lines could be found. Sixteen of the minerals, two of the mineral waters, and one of the meteorites were proved to contain helium, but if the gases extracted from them contained any gas other than helium or a trace of argon, it must have been in quantity too minute to have revealed itself to the spectroscope.

The gas which we were in search of was ultimately found in argon. The argon, amounting to about 15 litres, was prepared by means of apparatus, of which a description is given in the sequel. From the air employed in a liquid state for the purpose of liquefying and fractionally distilling the argon, two other elementary gases have been obtained, besides one yielding the "Swan" spectrum. A preliminary account of all these gases has already been given in the *Proceedings of the Royal Society* under the names of "Neon," or "new," "Krypton," or "hidden," and "Metargon," and at the meeting of the British Association at Bristol, the discovery of "Xenon" or "the stranger" was announced. The removal of these gases from argon has put us in possession of pure argon, and the present paper deals with some of its properties.

The Properties of Pure Argon.

In order to prepare 15 litres of argon, it is necessary to deal with about 1500 litres of atmospheric air, of which approximately 1200 litres consist of a mixture of nitrogen and argon. To absorb the nitrogen contained in this quantity of gas by conversion into nitride, 4 kilogrms. of magnesium would be required theoretically, but in order to cover loss through leakage and incomplete action, 5 kilogrms. of the metal are employed. The absorption of the oxygen and nitrogen was conducted in three stages. In the first, the oxygen was removed by means of metallic copper; in the second, the nitrogen was passed twice over metallic magnesium; and in the third, the gas, now rich in argon, was finally freed from nitrogen and hydrogen by passage over a mixture of anhydrous lime and magnesium powder heated to a red heat, and subsequently over red-hot copper oxide. The apparatus employed is shown in detail in the annexed figure.

It was of course necessary to confine the gas over water between the successive stages of purification, and finally to store the gaseous argon in the same way. On account of the considerable solubility of argon in water, this would have entailed no small loss if the quantity of water with which it had been brought into contact had been large. We consequently decided to make use of gas-holders of the gasometer type, in which the water was contained in an annular space of small capacity. Balance weights were attached to cords passing over pulleys, and served to relieve the pressure on the gas due to the weight of the gasometer. As the volume of the gas decreased after each successive stage, the four gas-holders employed were of

* A Paper read before the Royal Society, December 15, 1898.

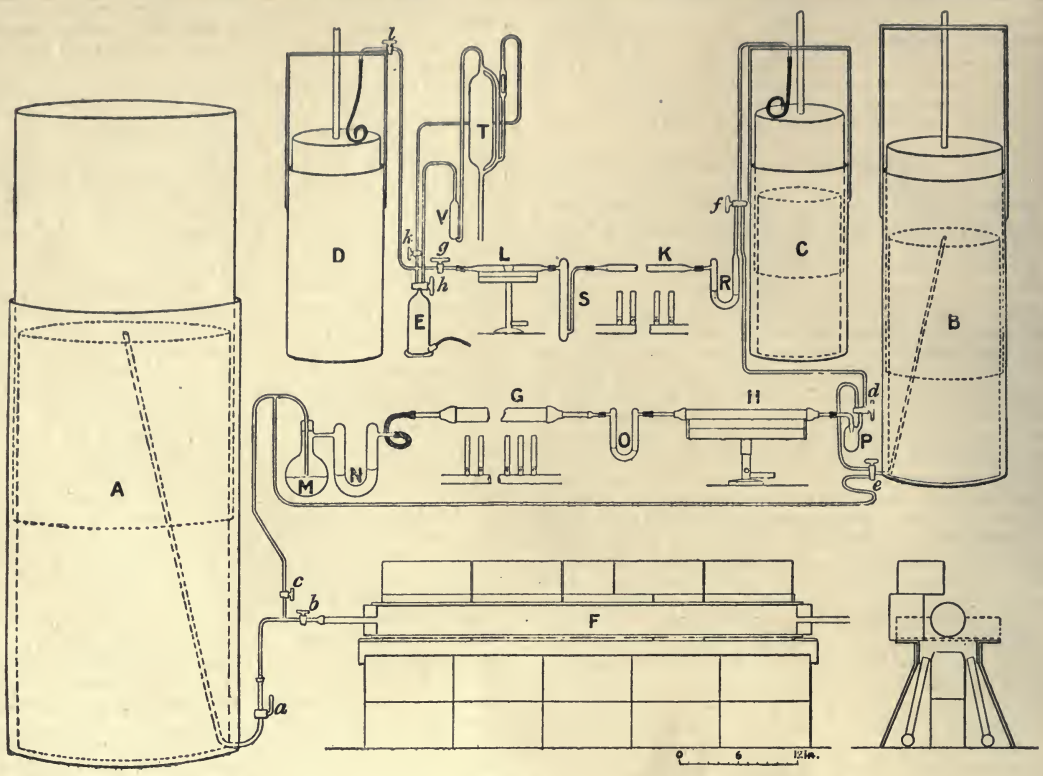

FIG. 2.

different sizes; the capacity of A was about 180 litres; that of B, 27 litres; and of C and D, each 18 litres.

Atmospheric nitrogen was obtained by drawing air, freed from carbon dioxide by passage through caustic soda solution, over heated metallic copper. A large iron tube F, 3 feet 6 inches long, and 3·5 inches in diameter, containing 25 lbs. of scrap copper, was connected with the gas-holder A; the tube was heated in a long fire-brick trough during these experiments, but a gas-furnace is shown in the figure, which has now been substituted for the more primitive arrangement.

The time required to fill the gas-holder was usually about five hours, and it was found, on analysis of the gas, that one single operation sufficed for the complete removal of all oxygen. The oxidised copper was reduced between each operation by means of coal-gas.

By closing the stop-cock *b*, and opening the stop-cock *c*, the gas-holder A could be placed in communication with the apparatus in which the preliminary absorption of nitrogen took place. By placing weights on the top of the gas-holder, the nitrogen was driven through the vessel M and the U-tube N, both of which contained strong sulphuric acid, into the tube G, which contained magnesium. This tube was a piece of steam-barrel, 1·5 inches in diameter, connected at each end by a reducing socket with an iron tube, 0·25 inch in diameter. The tube contained 250 grms. of magnesium, cut into coarse shavings in a shaping machine; the magnesium was not pressed very tightly into the tube. Since after each operation it was necessary to remove the sockets in order to clear the tube, the joints were luted with red lead, and the tube was made of sufficient length to project about 3 inches at each end of the furnace.

The greater part of the nitride was generally removed by using an iron rod, and the remainder by means of water, which converted it into the hydroxide. The tube was raised to a bright red heat before connecting it with the U-tube O, in order to allow the greater part of the hydrogen occluded by the magnesium to escape. The absorption of the nitrogen, which was indicated by the rate of flow of the gas through the U-tubes N and O, was maintained briskly until practically the whole of the magnesium was converted into nitride; the volume of the gas absorbed was equivalent to half the capacity of the large gas-holder.

The gas, after leaving the U-tube O, passed through a second iron tube H containing copper oxide; next, through the vessel P, in which water condensed; and it finally collected in the gasometer B. That which passed during the first stages of the process consisted of nitrogen containing much argon, but towards the end of the operation the argon became much diluted, until finally the gas which passed through the U-tube O consisted almost entirely of atmospheric nitrogen. The tube G was then replaced by another containing a fresh supply of magnesium.

The tap *c* was then closed, and the taps *d* and *e* turned, so that the gas in the gasometer B could be made to flow through the magnesium and copper oxide tubes into the gasometer C. In this process its volume was very much reduced, and the gas which collected in C probably contained as much as 25 per cent of argon. When the whole of the gas had been expelled from B, the taps *d* and *e* were again turned, and atmospheric nitrogen was allowed to flow through the magnesium tube, as in the first stage of this operation.

When the gasometer C had become full of the mixture of nitrogen and argon, as it did at the end of every third or fourth operation, it became necessary to reduce its volume by further absorption of nitrogen. The method employed, which was first described by Maquenne (*Compt. Rend.*, 1895, vol. cxxi., p. 1147), consisted in passing the gas through a hard glass tube containing a mixture of magnesium powder and lime, heated to a dull red heat in

a combustion furnace. The lime was obtained by thoroughly calcining precipitated chalk in a muffle. The nitrogen continued to be completely absorbed as long as calcium remained unattacked, so that the product of this operation consisted of pure argon. The gas issuing from the calcium tube passed through a tube S, containing soda-lime, and over copper oxide in the tube L, on its way to the gasometer D. Since at the end of the operation the system of tubes between the gas-holders C and D contained argon, in order to avoid loss, the circuit was placed in communication with a Töpler pump T, through the stop-cock *k*. The space between the stop-cocks *l* and *f* was exhausted at the commencement of the operation, the exhaustion being continued till the greater part of the hydrogen, which is always evolved when a mixture of magnesium and lime is heated, had been given off.

When it was necessary to suspend operations, the taps *l* and *f* were closed, the tap *k* was opened, and the argon was taken into the pump and delivered into the vessel V, which covered the upturned end of the capillary tube of the pump. From V the argon could be drawn into the small gas-holder E, which contained mercury, and which could also be placed in communication with the system through which the gas passed on its way from C to D.

These operations were repeated until the gasholder D contained about 15 litres of argon. The whole of this argon was then liquefied in an apparatus of which Fig. 2

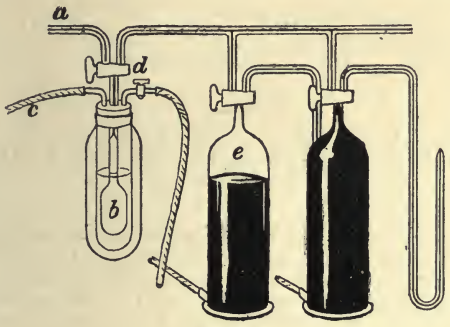

Fig. 2.

is a representation. The argon entered through the tube *a* into the bulb *b*, of some 25 c.c. capacity, surrounded by liquid air contained in a double-walled vacuum jacket. The air was made to boil under a low pressure of a few centimetres of mercury by means of a Fleuss pump attached to the tube *c*. The argon rapidly and completely liquefied to a colourless mobile liquid; it showed no absorption spectrum. Its volume was about 17·4 c.c. By turning the tap *d* it was placed in communication with the first of the series of mercury gasholders, *e*; the reservoir was then lowered so as to remove the lower-boiling portions of the liquid. During this distillation, which took place at constant temperature, the pressure on the boiling air was kept as low as possible. This gas subsequently turned out to be rich in neon, and to contain helium (*Roy. Soc. Proc.*, lxiii., 437). The remainder of the argon boiled back into the gasometer until the last few drops were left; the residue solidified, and finally gave a gas to which we gave the name metargon; it was collected in mercury gasholders (*loc. cit.*, p. 439). As will be subsequently shown, the krypton and xenon in this quantity of argon are too minute for detection. A similar operation for the purpose of separating the lighter as well as the heavier constituents was afterwards repeated three times, the middle portion of argon being always returned to the gasholder D (Fig. 1). A fourth liquefaction was carried out in which six mercury gasholders were filled with six separate fractions of argon, each taken after each successive fifth of the total argon had evaporated. These fractions were next purified from any nitrogen accidentally present by sparking with oxygen over caustic potash. After the removal of the oxygen the density was determined.

(To be continued).

DETERMINATION OF THE IODINE VALUE FOR FATTY MATTERS.

By C. ASCHMANN.

In the analysis of a fatty body, Hübl's method may give very valuable indications as to the purity of the substance under examination. Numerous modifications have been introduced to this method with a view to render it sufficiently exact, but this end has not yet been achieved.

To obtain concordant values for the iodine for one and the same fat or oil, it is necessary for the titration value of the iodised solution to remain constant, and that the duration of the reaction, the temperature, and the method of agitation should be identical in every experiment. As we well know, Hübl's solution is very unstable. Waller has removed this difficulty by suppressing it entirely. Now, I have succeeded in preparing a chloro-iodised solution which gives excellent results, and of which the value remains *constant*. The strength of my solution is such that it gives nearly the same figures as Hübl's freshly-prepared solution; these figures, however, relate to the volume, and not the weight of the fatty body. I have found, in fact, that weighing—and, above all, pouring oils from one glass to another—easily leads to errors. On the other hand, measurement by volume, as I propose, is simple and very exact.

Preparation of the Chloro-iodised Solution. — Thirty grms. of pure iodide of potassium are dissolved in 100 c.c. of water in a flask of 1 litre capacity and furnished with a lateral tube. Through this solution, a current of well-washed chlorine is passed. As soon as the iodine is deposited in the form of a voluminous loose mass, the flask should be agitated for the purpose of dissolving this iodine. When the solution is complete, chlorine should be again passed through the now deep yellow liquid for another two minutes. After standing for five or six hours in a cool place, the solution deposits a crystalline mass formed of a combination of iodic acid and iodate of potassium. If the crystallisation is slow in appearing, it is only necessary to throw into the solution a few crystals of iodate of potassium to cause it to start. The crystals are separated by filtration, washed, and the filtrate, with the washings, are together diluted up to 1 litre. From this chloro-iodised solution we prepare a titrated solution, of which 10 c.c. added to 10 c.c. of a solution of iodide of potassium (20 grms. KI to 100 c.c. of water) corresponds exactly to 40 c.c. of a decinormal solution of hyposulphite of soda (27·8 grms. per litre). The hyposulphite solution is controlled by a decinormal solution of iodine.

The chloro-iodised solution thus prepared will keep for years without changing.

Preparation of the Solution of the Fatty Substance.— In the case of liquid fatty matters, exactly 10 c.c. are taken with a pipette, the temperature being brought to 15° C., and allowed to run slowly into a flask fitted with a ground-glass stopper; the pipette must not be blown into. Into the same flask 10 c.c. of chloroform are run from a burette. To rinse the pipette, it is filled with the solution of the fatty substance in chloroform, and allowed to run out slowly, at the same time stirring the contents of the flask with the pipette. By repeating this operation three times, we eventually get a homogeneous solution. If we have to deal with solid or semi-fluid bodies, such as butter, tallow, or castor oil, they must be first heated to 50°. If the value of iodine is not determined immediately, the flasks containing the mixtures must be kept in a cool place away from the light.

Determination of the Titration Value of the Iodine.—I would first remark that I make no difference between siccative and non siccative oils. For measuring the chloroform solution of the fatty body I use a 1 c.c. burette divided into hundredths of a c.c. After having filled the burette by aspiration, I run 0·4 c.c. of of the solution into a flask of 250 c.c. capacity fitted with a ground-glass stopper. After waiting five minutes for the liquid which adheres to the surface of the pipette to run into the flask, I add 10 c.c. of chloroform. The 20 c.c. of the chloro-iodised solution which it is now necessary to add to the contents of the flask cannot be measured exactly with a burette; but concordant results can be obtained with a 20 c.c. pipette, which must be subsequently rinsed with 4 c.c. of water, which are also added to the contents of the flask.

The flask must now be carefully shaken, but care must be taken that the stopper is not wetted, or there would be a liability to errors. The flask is then plunged half-way into water at about 10° (9° to 11°) and kept there for twenty-four hours away from the light. During the first six hours the flask must be shaken six times at regular intervals. At the end of the twenty-four hours the titration is done in the ordinary manner.

Example: Linseed Oil.—Twenty c.c. of the chloro-iodised solution require 80 c.c. of the hyposulphite solution (10 c.c. = 0·127 I). After the action of the fatty matter the 20 c.c. of the chloro-iodised solution required only 67·8 c.c. of hyposulphite: 80 − 67 8 = 12·2.

$$\frac{12{\cdot}2 \times 0{\cdot}127}{10} = 0{\cdot}1549.$$

$$\frac{0{\cdot}1549 \times 100}{0{\cdot}2} = 77{\cdot}4 = \text{value of iodine.}$$

In the following table I have given the iodine values as determined by my method on several fatty substances I had at my disposal.

Fatty Substances of Vegetable Origin.

	Iodine value. Aschmann.	Hübl.
Olive oil (Nice)	77·4	78·5 to 84
„ (Genoa)	74·9	—
Poppy-seed oil	122 5	134 to 136
Oil of earth nuts	100·3	103
Sweet almond oil	95·0	98·4
Oil of sesamy	98 4	106
Linseed oil	142·8	148 to 158
Brown colza oil	92·7	100·4 to 1 2 8
White colza oil	92 7	—
Cotton-seed oil	104·7	106 to 110
Castor oil	81·28	84·4
Cocoa-nut oil	5 08	8 9 to 9·4

Fatty Substances of Animal Origin.

Cod-liver oil (from the Indies)	1 6 0	—
„ white	133·3	—
„ brown	128 2	—
Tallow	52·0	57·1 to 60
Beef fat	35 5	40 to 44
Goat butter	24 1	—

Margarines.

	Iodine value (Aschmann).
1.	50·8
2.	63·5
3.	57·2
4.	55·2
5.	56·5
6.	58·4
7.	55·9

Butters.

1.	From the Milk Company		33·60	(26·0 to 35·1
2.	„	„	33 60	according to
3.	„	„	36·50	Hübl).
4.	„	„	35·50	
5.	„	„	37·90	
6.	„	„	34·90	
7.	„	„	34·90	
8.	„	„	36·20	
9.	„	„	34 90	
10.	„	„	35 50	
11.	„	„	36·20	
12.	Butter from the Market		42 50	
13.	„	„	31·75	
14.	„	„	31 20	
15.	„	„	36·20	
16.	„	„	31·10	
17.	„	„	35 50	
18.	„	„	32 30	
19.	„	„	31·10	
20.	„	„	31·20	
21.	„	„	29 80	
22.	„	„	34 90	
23.	„	„	29 80	
24.	„	„	36 50	
25.	„	„	38·70	

—*Chemiker Zeitung*, p. 59, 1898.

UNIFORM METHODS FOR THE ANALYSIS OF FATTY BODIES.

By F. ULZER.

Index of Acidity.—By reason of the variations of the index of acidity according to the nature of the fatty body under examination, it is impossible to fix *à priori* the weight of the sample to work upon. This must be taken approximately in inverse ratio to the value of the index of acidity. As a rule we work on from 5 to 10 grms. The fat must be dissolved in ether, to which is added an equal volume of alcohol, and titrated with an aqueous or alcoholic solution of demi-normal soda (or deci-normal if the acidity is low), in the presence of phenolphthalein. If the acidity is very low 20 or 30 grms. of the sample may be taken, add 100 c.c. of perfectly neutral alcohol, shake carefully, and titrate with demi-normal soda.

Index of Saponification.—In preparing the alcoholic potash it is necessary to follow Henrique's instructions, and boil the powdered potash with alcohol at 95° in a flask fitted with a vertical condenser. If dilute alcohol is used the results will not be in concordance.

There are two methods of saponification:—

1. *Warm Saponification.* — 2 to 2·5 grms. of the substance are treated with 25 c.c. of demi-normal potash and 25 c.c. of alcohol; boil for half an hour in a flask fitted with a vertical condenser, and titrate the excess of alkali with demi-normal hydrochloric acid. In the case of waxes it is necessary to add 10 c.c. of petroleum ether boiling at 100° C.

2. *Cold Saponification.*—There are two cases to consider:—

a. Neutral Fats.—We dissolve 3 or 4 grms. of the substance in 25 c.c. of cold petroleum ether, add 25 c.c. of a deci-normal solution of soda, shake well, and allow to stand for twelve hours at the ordinary temperature, and titrate as in the former case,

b. Waxes.—We use warm petroleum ether, and add soda lye immediately; heat to complete the solution, and allow to stand for twenty-four hours. Finally we titrate with demi-normal hydrochloric acid, taking care to heat the solution several times during the titration. The petroleum ether used should not boil below 100° C.

Index of Iodine.—As good results are obtained with Hübl's as with Waller's reagent. If we arrange that the

excess of iodine be kept at double the amount of iodine absorbed, the time of the reaction will not exceed six hours. The solution of iodine, which should be prepared forty-eight hours before it is used, must be of such a strength that 25 c.c. of this solution will require at least 35 c.c. of decinormal hyposulphite for its saturation. For siccative oils and fish oils we use 0·1 to 0·2 grm., for non-siccative oils 0·2 to 0·25 grm., for suet fats 0·5 grm., and for palm oil or cocoa-nut oil about 1 grm. The substance is dissolved in 15 c.c. of pure chloroform, we add 25 c.c. of the iodine solution, and let stand for six hours. For titrating we use 25 c.c. of a 10 per cent solution of iodide of potassium. If there are a large number of determinations to make it is preferable, before commencing the back titration, to determine by a check experiment if the strength of the solution has varied, and to what degree. Account must be kept of this variation in calculating out the results. The conditions of the operation are exactly the same for Hübl's reagent as for Waller's.—*Chem. Rev. Fett. u. Harz. Ind.*, iv., [22], p. 299.

RESEARCH ON COMMERCIAL INCANDESCENT GAS MANTLES.

By E. HINTZ.

The author has already shown that the lighting power of mantles containing 99 per cent of oxide of thorium, and 1 per cent of oxide of cerium, was not influenced by the addition of 1 per cent of oxide of neodymium, lanthanum, or yttrium, or by the addition of 0·2 to 1 per cent of oxide of zirconium, while the effect of even 2 per cent of oxide of zirconium remained doubtful.

Following up his researches the author has obtained a large number of interesting results, which are here given in brief. In the following lines the normal mixture of 99 parts of oxide of thorium, and 1 part of oxide of cerium, will be called "thorium-cerium."

The following are the general conclusions arrived at:—

1. The addition of less than 0·2 per cent of oxide of zirconium to the thorium-cerium does not influence its lighting power. From this point of view then, oxide of zirconium can be classed with the other oxides.

2. When we add to the thorium-cerium a maximum of 2 per cent of neodymium, lanthana, or yttria, the lighting power is not affected, but it is slightly lowered by the addition of 2 per cent of oxide of zirconium.

3. In the presence of larger proportions of foreign oxides, the lighting power of the thorium-cerium mantles is nearly always diminished. A large proportion of neodymium or of yttria is more prejudicial than an equal quantity of zirconia or lanthana.

Table I. contains some characteristic results on this subject:—

Table I.

Composition of the mantles.	Maximum lighting power in Hefner units.	Consumption of gas in litres per hour.	
		Total.	Per Hefner unit.
Thorium-cerium .. 95 Zirconia 5	43	123	2·9
Thorium-cerium .. 80 Zirconia 20	50	105	2·1
Thorium-cerium .. 95 Neodymium 5	66	120	1·8
Thorium-cerium .. 80 Neodymium 20	40	143	3·6
Thorium-cerium .. 95 Lanthana 5	73	135	1·9
Thorium-cerium .. 80 Lanthana 20	54	124	2·3
Thorium-cerium .. 95 Yttria 5	62	126	2·0
Thorium-cerium .. 80 Yttria 20	38	121	3·2

Effects Produced by Varying the Proportions of Thorium and Cerium.—To prepare oxide of thorium ThO_2 in a state of purity, the thorite was decomposed by hydrochloric acid, and the solution treated with sulphuretted hydrogen, and then with oxalic acid according to the now well-known method.

The precipitated oxalates were digested with oxalate of ammonia; the solution was considerably diluted, left to stand for some time, and filtered. The oxalates were re-precipitated by acidulating the filtered liquid with hydrochloric acid. Finally they were successively transformed into oxides, sulphates, hydrates, and chlorides; the slightly acid and dilute solution of the chlorides was precipitated by hyposulphite of soda; the precipitate was re-dissolved in hydrochloric acid, re-precipitated, and again dissolved in hydrochloric acid. The hydrate of thorium was finally precipitated with ammonia, and then transformed into nitrate. The solution contained 14·5 per cent of the oxide ThO_2.

A solution of pure oxide of cerium was also prepared, and it was into a suitable mixture of the two solutions that the tissue was plunged. The mantles were incinerated for from twenty-five to fifty minutes before being tested.

In Table II. are given the most interesting observations made by the author:—

Table II.

Composition of the mantles.	Lighting power in Hefner units.	Consumption of gas in litres per hour.	
		Total.	Per Hefner unit.
Pure oxide of thorium ..	2·6	130	50
Pure oxide of cerium ..	2·0	125	61
Oxide of thorium .. 99·9 ,, cerium .. 0·1	17·0	115	6·7
,, thorium .. 99·8 ,, cerium .. 0·2	41·0	129	3·1
,, thorium .. 99·5 ,, cerium .. 0·5	62·0	133	2·1
,, thorium .. 99·0 ,, cerium .. 1·0	71·0	101	1·4
,, thorium .. 98·0 ,, cerium .. 2·0	61·0	101	1·7
,, thorium .. 97·0 ,, cerium .. 3·0	50·0	101	2·0
,, thorium .. 95·0 ,, cerium .. 5·0	40·0	101	2·4
,, thorium .. 90·0 ,, cerium .. 10·0	11·0	101	9·5
,, thorium .. 80·0 ,, cerium .. 20·0	8·4	101	12·0
,, thorium .. 60·0 ,, cerium .. 40·0	3·3	101	31·0
,, thorium .. 30·0 ,, cerium .. 70·0	2·2	103	48·0

With regard to the constancy of the lighting power the following facts were observed:—

A mantle containing 99·9 per cent of oxide of thorium, and 1 per cent of oxide of cerium, and giving 17 Hefner units at the first, with a consumption of gas of 115 litres per hour, gave, after 800 hours burning, 7·5 Hefner units, with a consumption of 114 litres of gas per hour. Another mantle containing 99·5 per cent of oxide of thorium, and 0·5 per cent of oxide of cerium, giving at first 40 Hefner units, with a consumption of 115 litres of gas per hour, gave, after burning 400 hours, a light of 27 Hefner units, with an hourly consumption of 116 litres of gas, and at the end of 800 hours its lighting power had fallen to 22 units for a consumption of 115 litres of gas per hour. Finally, a mantle containing 99 per cent of oxide of thorium, and 1 per cent of oxide of cerium, give, at these times, 54 units with 115 litres, 38 units with 116 litres, and 32 units with 114 litres.—*Zeitschrift für Analytische Chemie*, xxxvii. [8], p. 504.

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 29).

It remains only, as far as zincic oxide is concerned, to show how wide a difference in the amount of gas may be caused by the original mode of preparation of the solid material.

The Effect of Physical Condition upon the Total Amount of Gas retained by Zincic Oxide.

	C.c. gas.
53. 1 grm. of ZnO, prepared from zincic carbonate at 880°, gave	0·00
54. 1 grm. of ZnO, prepared from zincic carbonate at 880°, gave	0·00
Average	0·00
55. 1 grm. of ZnO, prepared from the nitrate at 280°, not ignited, gave	0·01
56. A similar experiment gave	0·02
Average	0·015
57. 1 grm. of ZnO, prepared from zincic nitrate, but heated to 880° in a slightly reducing atmosphere, gave	0·05
58. A similar experiment gave	0·15
Average	0·10
42. 1 grm. of ZnO, prepared by gentle heating of the nitrate at 280°, and subsequent ignition for 30 minutes at 880° in an oxidising atmosphere, gave	0·192
43. A similar experiment gave	0·192
Average	0·192
59. 1 grm. of similar ZnO, prepared in the same way, but heated to 670° for 3 hours and then preserved two weeks before heating ½ hour at 880°, gave	0·292
60. A similar experiment gave	0·260
Average	0·276
61. 1 grm. of more compact ZnO, prepared by heating the nitrate rapidly, and having been preserved for two weeks before being ignited for ½ hour at 880°, gave	0·387
62. A similar experiment gave	0·396
Average	0·392

The evidence of these results proves that the total amount of gas retained by zincic oxide varies with every detail of the method of preparation; hence this amount cannot serve as a sure guide to the temperature of ignition, unless a perfectly uniform sample is used for all trials.† Of course the amounts of nitrogen found in these samples varied widely; for the gas resulted from the decomposition of zincic nitrate, which was imprisoned in varying quanitties according to the physical condition of the zincic oxide.

Since so many circumstances regulate both the amount of gas and its composition, one is not surprised that Morse and Arbuckle obtained varying mixtures with eight different preparations of zincic oxide. It is true that their expulsion of the gases continued until it had become so slow that two successive weighings with intermediate heating gave constant weight; but the same causes of change must still have been at work, although far more slowly.

In the light of these interesting results, it seemed worth while to make a more elaborate investigation of the relation of the composition of the gases held by *cupric* oxide to the temperature used in its ignition. The material used in the following determinations was the soft powder made by the decomposition of cupric nitrate at 280°.

The Effect of Temperature of Ignition on the Composition of Gases retained by Cupric Oxide.

Time of Ignition, 1 hour.

	Per cent oxygen.
63. 0·32 c.c. gas from 1 gr. CuO heated at 520° contained	18
64. 0·34 „ „ „	15
Average	15·5
65. 0·49 c.c. gas from 1 gr. CuO, heated at 660° contained	6
66. 0·48 „ „ „	5
Average	5·5
67. 0·47 c.c. gas from 1 gr. CuO, heated at 750° contained	3
„ „ „ „	4
Average	3·5

0·05 c.c. gas from 1 gr. CuO, heated at 1000°± contained 0 to 4 per cent oxygen, according to Alexander Scott.

It is evident that the cupric nitrate remaining in the cupric oxide had not been wholly decomposed by heating for an hour at 500° (experiments Nos. 63 and 64), and that we are dealing here with an increasing total, and a maximum similar in every respect to that already noted in the case of zinc, except that in the present case more nitrogen is held, while the oxygen escapes at a much lower temperature.

The Effect of Time on the Composition of the Gas retained by Cupric Oxide.

First Series: Temperature, 500°.
(Argentic Chloride easily melted; Plumbic Chloride scarcely melted).

	Per cent oxygen.
68. 0·29 c.c. gas from 1 gr. CuO, heated 2 hours contained	25
69. 0·29 „ „ „	23
Average	24
70. 0·38 c.c. gas from 1 gr. CuO, heated 8 hours contained	15
71 0·42 „ „ „	14
Average	14·5
72. 0·46 c.c. gas from 1 gr. CuO, heated 16 hours contained	8

Second Series: Temperature, 520°.
(Just below the melting-point of Argentic Iodide, but distinctly above that employed in the last series).

73. 0·15 c.c. gas from 1 gr. CuO, heated for 15 min., contained	23
63. 0·32 c.c. gas from 1 gr. CuO, heated for 1 hr., contained	18
64. 0·34 „ „ „	15
Average	16·5

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 22; also *American Chemical Journal*, November, 1898.

† Small quantities of such impurities as alkali and silica do not seem to affect the occlusion, however. See *Proc. Amer. Acad.*, xxviii., 207.

	Per cent oxygen.
74. 0·48 c.c. gas from 1 gr. CuO, heated for 2 hrs., contained	12
75. 0·40 c.c. gas from 1 gr. CuO, heated for 16 hrs., contained	6

Third Series: Temperature, 600°.
(Argentic Iodide fused easily; Lithic Chloride fused slowly).

76. 0·43 c.c. gas from 1 gr. CuO heated for 10 min., contained	12
77. 0·38 „ „ „	12
Average	12
78. 0·46 c.c. gas from 1 gr. CuO, heated for 20 min., contained	13
79. 0·53 c.c. gas from 1 gr. CuO, heated for 35 min., contained	10
80. 0·51 „ „ „	8
Average	9

Fourth Series: Temperature, 640°.
(Thallous Sulphate just fused; Strontic Nitrate remained solid).

81. 0·21 c.c. gas from 1 gr. CuO, heated for 2 mins., contained	35
82. 0·19 „ „ „	36
Average	35·5
83. 0·43 c.c. gas from. 1 gr. CuO, heated for 10 min., contained	19
84. 0·45 „ „ „	16
Average	17·5
85. 0·46 c.c. gas from 1 gr. of CuO, heated for 8 hrs., contained	6
86. 0·45 „ „ „	4
Average	5

It is clear that we are dealing here with a phenomenon precisely similar to that observed in the case of zinc. The decomposition of the remaining traces of nitric anhydride takes place much more slowly at low temperatures than at high ones, and the oxygen formed by this decomposition is liberated far more rapidly during the hotter ignitions.

A single series of experiments (*Proc. Amer. Acad.*). xxviii., 209), made some years ago with magnesic oxide), shows that this substance too acted in the same way, and it is probable that all the other oxides retaining traces of occluded gases would give similar results. The data obtained from magnesic oxide are repeated below, in order that all the facts may be at hand for the following consideration of the causes of the anomaly.

Gas Evolved from Magnesic Oxide.

(Temperature of Ignition was about 700°—800°.

1 grm. MgO after ignition 30 minutes gave 3·60 c.c. nitrogen and 7·2 c.c oxygen.
1 grm. MgO after ignition 60 minutes gave 4·72 c.c. nitrogen and 6 3 c.c. oxygen.
1 grm. MgO after ignition 75 minutes gave 4·84 c.c. nitrogen and 4·4 c.c. oxygen.
1 grm. MgO after ignition 135 minutes gave 5·44 c.c. nitrogen and 3·6 c.c. oxygen.
1 grm. MgO after ignition 195 minutes gave 5·24 c.c. nitrogen and 2·8 c.c. oxygen.

(To be continued).

DERIVATIVES OF THE TETRACHLORIDES OF ZIRCONIUM, THORIUM, AND LEAD.*

By J. MERRITT MATTHEWS.

(Concluded from p. 33).

H. *Quinoline.*

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 2C_9H_7N$.—0·6140 grm material gave:—

0·6977 grm. silver chloride = 0·1727 grm. chlorine = 28·12 per cent chlorine.

0·1592 grm. zirconium dioxide = 0·1177 grm. zirconium = 19·17 per cent zirconium.

0·7226 grm. material gave:—

0·0478 grm. ammonia = 0·0394 grm. nitrogen = 5·45 per cent nitrogen.

	Calculated for $ZrCl_4 \cdot 2C_9H_7N$.	Found.
Chlorine	28·94	28·12
Zirconium	18·47	19·17
Nitrogen	5·72	5·45

b. Thorium Tetrachloride, $ThCl_4 \cdot C_9H_7N$.—0·4110 grm. material gave:—

0·4634 grm. silver chloride = 0·1147 grm. chlorine = 27·91 per cent chlorine.

0·2175 grm. thorium dioxide = 0·1911 grm. thorium = 46·50 per cent thorium.

0·4212 grm. material gave:—

0·0129 grm. ammonia = 0·0106 grm. nitrogen = 2·52 per cent nitrogen.

	Calculated for $ThCl_4 \cdot C_9H_7N$.	Found.
Chlorine	28·19	27·91
Thorium	46·18	46·50
Nitrogen	2·78	2·52

c. Lead Tetrachloride, $PbCl_4 \cdot 2C_9H_7N$.—Quinoline reacted very energetically with lead tetrachloride, yielding a lemon-yellow precipitate which proved to be quite stable.

0·3012 grm. material gave:—

0·2806 grm. silver chloride = 0·0695 grm. chlorine = 23·06 per cent chlorine.

0·2298 grm. material gave:—

0·1140 grm. lead sulphate = 0·0779 grm. lead = 33·90 per cent lead.

0·2792 grm. material gave:—

0·0845 grm. platinum = 0·0121 grm. nitrogen = 4·34 per cent nitrogen.

	Calculated for $PbCl_4 \cdot 2C_9H_7N$.	Found.
Chlorine	23·39	23·06
Lead	34·10	33·90
Nitrogen	4·61	4·34

I. *β-Naphthylamine.*

a. Zirconium Tetrachloride, $ZrCl_4 \cdot 2C_{10}H_7NH_2$.—On adding a solution of naphthylamine in anhydrous ether to a solution of zirconium tetrachloride a greyish brown precipitate was produced, the analysis of which approximated to the formula given above.

0·5736 grm. material gave:—

0·6419 grm. silver chloride = 0·1589 grm. chlorine = 27·70 per cent chlorine.

0·1397 grm. zirconium dioxide = 0·1032 grm. zirconium = 18·00 per cent zirconium.

0·7012 grm. material gave:—

0·0426 grm. ammonia = 0·0351 grm. nitrogen = 5·01 per cent nitrogen.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx., No. 11. From author's thesis for the Degree of Doctor of Philosophy.

	Calculated for $ZrCl_4 \cdot 2C_{10}H_7NH_2$.	Found.
Chlorine	27·38	27·70
Zirconium	17·47	18·00
Nitrogen	5·41	5·01

b. Thorium Tetrachloride, $ThCl_4 \cdot C_{10}H_7NH_2$. — This derivative was greyish white in colour and comparatively stable in the air.

0·2582 grm. material gave :—
0·2844 grm. silver chloride = 0·0704 grm. chlorine = 27·27 per cent chlorine.
0·1329 grm. thorium dioxide = 0·1168 grm. thorium = 45·25 per cent thorium.

0·6045 grm. material gave :—
0·0166 grm. ammonia = 0·0137 grm. nitrogen = 2·27 per cent nitrogen.

	Calculated for $ThCl_4 \cdot C_{10}H_7NH_2$.	Found.
Chlorine	27·43	27·27
Thorium	44·94 ..	44·25
Nitrogen	2·70	2·27

c. Lead Tetrachloride, $PbCl_4 \cdot C_{10}H_7NH_2$.—Naphthylamine gave a dark green precipitate with lead tetrachloride in a dilute solution; in more concentrated solutions the naphthylamine was apparently decomposed.

0·2276 grm. material gave :—
0·2604 grm. silver chloride = 0·0645 grm. chlorine = 28·32 per cent chlorine.

0·3006 grm. material gave :—
0·1914 grm. lead sulphate = 0·1307 grm. lead = 43·47 per cent lead.

0·2416 grm. material gave :—
0·0544 grm. platinum = 0·0079 grm. nitrogen = 3·24 per cent nitrogen.

	Calculated for $PbCl_4 \cdot C_{10}H_7NH_2$.	Found.
Chlorine	28·86	28·32
Lead	42·07	43·47
Nitrogen	2·84	3·24

J. *Acid Amides.*

The action of acetamide and benzamide was tried on the solutions of the tetrachlorides, but no compound resulted in any case, the acid amides evidently not being sufficiently basic to form derivatives like the amines.

Diphenylamine was also tried, but it gave no reaction with either the zirconium or thorium salt. The lead salt gave a deep blue solution and lead chloride separated out, showing that the lead tetrachloride in this case acted like bleaching lime on diphenylamine.

5. General Remarks.

On comparing the derivatives of the three tetrachlorides here used, many similarities will at once be evident. In order to facilitate with such a comparison it will not be superfluous to present a tabular *résumé* of the various derivatives herein prepared and described.

	With $ZrCl_4$. Mols. amine.	With $ThCl_4$. Mols. amine.	With $PbCl_4$. Mols. amine.
Ammonia (from solution)	8	8	4, 2
Ammonia (without heat).	2	6	
Ammonia (with heat) ..	4	6	
Methylamine	4	4	4
Ethylamine	4	4	4
Propylamine	4	4	4
Aniline	4	4	3
Toluidine	4	3	Decomp.
Pyridine	2	1	2
Quinoline	2	1	2
Naphthylamine	2	1	1
Diphenylamine ..	No reaction.	No reaction.	Decomp.
Acid amides			No reaction.

Nearly all these derivatives are stable in the air, the only noticeable exceptions being the pyridine, quinoline, and the lower ammonia compounds of zirconium and thorium. None of them show any tendency toward a crystalline structure, but come down as amorphous precipitates resembling hydroxides.

On heating these compounds in the air they readily split up into the amine hydrochloride and the dioxides; with lead, however, lead dichloride is left on ignition. They are also decomposed when treated with water, and the fixed alkalis precipitate the hydroxides of the three metals.

It will also be noticed that the majority of these derivatives seem to obey the law of Remsen in its application to molecular compounds; and the tendency is apparently toward an even number of molecules, though several of the thorium and lead derivatives deviate from this general law in having an odd number of additive molecules.

Two of the chlorine atoms in lead tetrachloride are very loosely combined, splitting off at the slightest disturbance to the chemical equilibrium of the compound; and yet it is of interest to note that the amines seem to fix these two atoms of chlorine into a more stable form, doubtless due to some peculiar internal linking in the compound. That these two atoms of chlorine are exceedingly active is seen by the behaviour of lead tetrachloride with toluidine, where no additive compound could be obtained, as the amine was decomposed even with dilute solutions, giving rise no doubt to complex chlorinated and condensed products. In fact, concentrated solutions of lead tetrachloride will decompose any of the aromatic amines, with the production of blue, purple, and green coloured solutions and resinous products. In this great activity of two of its atoms of chlorine, lead tetrachloride differs widely from the corresponding salts of zirconium and thorium, as these latter show no tendency to break down to lower chlorides.

THE OCCURRENCE OF COPPER IN THE PLANT WORLD.

By G. B. FRANKFORTER.

It has frequently been stated that the metal copper occurs in both plants and animals. Neubauer (*Zeit. Anal. Chem.*, v., 260) found, on careful examination, that animal tissue invariably contained a very small quantity of copper. He found, on analysing the tissue of various carnivorous animals, that 1 grm. of ash from the tissue contained from one- to two-tenths of a m.grm of copper. Bergeron and l'Hôte (*Comptes Rendus*, lxxx., 268) confirmed the above statement, giving special attention to the organs of the Mammalia. They invariably found copper in the liver and kidneys in comparatively constant quantities.

Ulex (*Journ. Prakt. Chem.*, xcv., 367; xcvi., 460) made an exhaustive examination of the tissue of various animals, and found copper in every instance. His experiments, however, were repeated by Lossen, who reached entirely different conclusions. Lossen showed that the copper found by Ulex came entirely from the Bunsen burner and other utensils containing copper with which he performed his experiments. So careful were his analyses that it seems impossible to doubt his conclusion. It seems possible, therefore, that the copper found by Neubauer and others may have come from similar sources. At any rate, it remains for future experiments to determine the exact extent of copper in the animal world.

Several announcements have been made of the occurrence of copper in the plant world. The general conclusion has been that plants growing on soil which contains copper, assimilate small quantities. Dieulafait (*Ann. Chim. et de Phys.* [5], xviii., 349), in an exhaustive treatise

on the distribution of copper in the primordial rocks, found copper widely distributed, ranging in quantity from a mere trace to great beds of the metal. He likewise showed that certain of the carbonate rocks contained appreciable quantities of the metal. The dolomites were invariably found to contain copper, while the lime carbonates were nearly always free from the metal. In a second paper (*Ann. Chim. et de Phys.* [5], xix. 550) Dieulafait showed that plants growing on a dolomitic soil, as well as a soil from the primordial rocks, contained an appreciable quantity of copper, while those growing on a limestone soil rarely ever contained a trace of copper.

There can be little doubt, at the present time, concerning Dieulafait's conclusion as to the distribution of copper in the various rocks. His conclusion as to its distribution in plants, however, remains somewhat uncertain, and much must be done before his conclusion may be fully and logically reached.

An interesting instance of the occurrence of copper in the plant world, however, came under my observation recently. While removing an oak tree which grew within the limits of the city of Minneapolis, and which had recently died, a gentleman noticed, in cutting up the trunk, a considerable quantity of bright copper-coloured powder disseminated through the pores of the wood. A quantity of this powder was examined, and found to be pure metallic copper. This strange coincidence led to a series of analyses of the different parts of the tree. A careful preliminary examination, preparatory to the analysis, showed certain parts of the tree to be thoroughly impregnated with this granular copper powder. Some of these granules were so large as to take on the form of flakes. The larger ones were partly rolled up so as to fit in the irregular pores of the wood. When unrolled, the large flakes measured 1½ m.m. in diameter.

The powder was then analysed, giving the following results:—

0·0608 grm. of the powder gave 0·0578 grm. of copper.
Per cent of copper 95·01.

In the microscopic examination of the powder a very small quantity of a white crystalline substance was observed, but the quantity was too small for an examination. Could these fine crystals have been removed, the copper would undoubtedly have been found unusually pure.

An Examination of the Wood.

In order to determine how thoroughly the copper was disseminated throughout the whole tree, a microscopical examination and several analyses were made. The microscopical examination revealed the fact that only the outer annual rings contained an appreciable quantity of the metal. The last six or seven annual rings were so full of these flakes of copper that they could easily be discerned by the naked eye. The earlier rings showed only a trace under the microscope and by analysis, and those nearest the heart were quite free from the metal.

The first conclusion was that, the soil here being dolomitic, the tree had assimilated copper from that source. The above facts plainly show that such cannot be the case, else the copper would be evenly distributed throughout the different parts of the tree. The following analyses serve to show how unevenly the metal was distributed through the wood:—

Analysis No. 1.—Wood taken from the heart of the tree: 500 grms. of wood gave 4·6 grms. of ash and 0·004 grm. of copper.

Analysis No. 2.—Wood taken from the tree about halfway between the heart and bark: 300 grms. gave 3·765 grms. of ash and 0·0056 grm. of copper.

Analysis No. 3.—Wood taken from near the bark: 200 grms. gave 2 86 grms. of ash and 0·0079 grm. of copper.

Analysis No. 4.—Wood taken representing an average of the whole tree: 350 grms. of wood gave 3·84 grms. of ash and 0·0042 grm. of copper.

Analysis.	Per cent of ash.	M.grms. of copper per 100 grms. of wood.
No. 1.	0·92	0·8
No. 2.	1·28	1·86
No. 3.	1·43	3·95
No. 4.	1·1	1·2

In these analyses every precaution was taken to eliminate any possibility of error from apparatus used. It would seem, from the uneven distribution of the copper, that the tree was not accustomed to such quantities of the metal, and that it had absorbed the metal within the last few years, a probable cause of its death.

The origin of the copper has not yet been determined. Native copper occurs here in the soil, and that at present would seem to be the most reasonable explanation of its source. If such is the case, then the plants of the Lake Superior Region, where native copper is still more abundant, should contain considerable quantities of copper. Experiments will be conducted along this line, in order to determine whether or not this occurrence is common there.

The fact that copper was found here in the metallic state raises the question of the form in which it exists in plants in general. Although nothing has been done along this line, it is reasonable to suppose that the metal is taken up in the form of some soluble salt. The genera form in which it left in plants must be determined by future experiments,

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Minneapolis.

CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.*

By A. B. PRESCOTT and H. M. GORDIN.

(Continued from p. 31).

Verification of the Equation for the Iodine Factor.

Partly from the fact that Kippenberger (*Ztschr. Anal. Chem.*, xxxv., 10; xxxiv., 317: on this question also see Gomberg, 1896; *Journ. Am. Chem. Soc.*, xviii., 332) has proposed a different reaction in the formation of periodide precipitates, and for other reasons, we thought it advisable to prove irrefutably that the iodide of potassium of the iodine solution takes an active part in the reaction by which the atropine enneaiodide, as an example, is formed and gives off an amount of iodine which is just equal to the amount of the normal iodine of the enneaiodide.

We proceeded in the following manner:—We first determined the strength of our iodine solution with regard to free iodine; this was done by means of a sodium thiosulphate solution of known strength. We then took 10 c.c. of this iodine solution and determined the total amount of iodine, free as well as bound to potassium, by shaking them in a flask with an excess of powdered metallic zinc till the colour of iodine disappeared, filtering the solution of zinc iodide and potassium iodide thus obtained, washing the flask and the excess of zinc with hot water, and precipitating the iodides in the filtrate with silver nitrate and nitric acid. From the weight of silver iodide washed and dried in the usual way, we calculated the amount of total iodine present in our iodine solution. By subtracting the amount of free iodine from that of the total iodine, we obtained the amount of iodine present in our solution as potassium iodide. We thus found that the iodine solution contained 1 per cent free iodine and 1·2312 per cent combined iodine.

We then put 40 c.c. of this iodine solution in a 100 c.c. measuring flask, added 20 c.c. of a 3/10ths per cent solution of atropine alkaloid, and, after shaking well, diluted

* *Journal of the American Chemical Society*, xx., No. 9, Sept., 1898.

the liquid in the flask to 100 c.c. We now took two phials, and in each filtered off 25 c.c. from the flask. In the first phial, the amount of free iodine titrated back with sodium thiosulphate was found to be 0·0465. From this it is easy to deduce that the 20 c.c. of the 3/10ths per cent atropine solution consumed 0·214 grm. of the free iodine. In the second phial the total iodine was determined in the same way as described above, and the quantity of silver iodide was found to be 0·3023 grm., which shows that after the treatment with atropine the liquid contained 1·633 per cent total iodine. From these data we deduce that the 20 c.c of the atropine solution have taken up 0·02528 grm. iodine from the bound iodine. As the 20 c.c. of atropine solution contained 0·06 grm. atropine, we find for 100 parts of precipitated enneaiodide:—

	Found. Per cent.	Calculated. Per cent.
Atropine..	20·05	20·26
Iodine taken from the free iodine of the iodine solution	71·50	70·88
Iodine from the iodine bound as KI	8·45	8·86

We see that in aqueous acidulous solutions the potassium iodide takes an active part in the reaction by joining in a yield of hydriodic acid for the normal hydriodide of the alkaloid, necessary to hold the additive iodine of the periodide. When carbon disulphide or carbon tetrachloride is used as a solvent for the atropine and the iodine, no periodide seems to be formed, possibly for the reason of there being no generation of hydriodic acid for the making of hydriodide. As to the formation of the periodides in chloroformic solution of atropine and iodine, it might possibly be explained by the substituting action of iodine either upon the chloroform or upon a side-chain of the atropine.

The direct substitution of iodine for some of the hydrogen in these bodies might, in this case, be made possible by the presence of the natural base, which combines with the hydriodic acid when formed by such a substitution. Part of the atropine would then act in a manner similar to that of mercuric oxide, which is usually employed in the iodising of hydrocarbons. An analogous case we have in the easy substitution of iodine for some of the hydrogen in aniline, a part of which combines with the hydriodic acid which is set free through the substitution of iodine for hydrogen in another part. At any rate we shall endeavour to determine the by-products formed when atropine enneaiodide is produced in chloroformic solutions.

Procedure in the Volumetric Method.

The general mode of procedure in the estimation of the strength of an aqueous solution of an alkaloidal salt is as follows:—To about 10 c.c. of decinormal iodine solution diluted with a little water, 1 c.c. of the acidulated alkaloidal solution is added, and the mixture well shaken for a few minutes. Should the precipitate separate out very quickly, and the clear supernatant liquid have only a light yellow or greenish colour, or be altogether colourless, the alkaloidal solution is too strong and must be diluted, till after a few trials the clear supernatant liquid retains a very dark red colour after the separation of the precipitate. The acidulated alkaloidal solution is then made up to a given volume, and 10 or 15 c.c. of it are run from a burette into a graduated vessel, into which has been previously put 25 or 30 c.c. decinormal iodine solution diluted with a little water. The mixture is then made up to a given volume and shaken till the supernatant liquid is perfectly transparent, and is of a very dark red iodine colour. This point is very important, and should the clear liquid not have this dark red colour the experiment with most alkaloids (except morphine and possibly some others, should be repeated, putting more decinormal iodine into the graduated vessel, or decreasing the number of c.c. of the alkaloidal solution. It would not do to add more decinormal iodine to the same mixture, as the iodine must be in large excess during the whole operation, in order to prevent the formation of lower periodides, which, once formed, might not take up fresh iodine and form higher periodides. Only with morphine, which in such solutions forms but one periodide, these precautions are unnecessary. When the liquid has become perfectly clear an aliquot portion of it is filtered off, and the excess of iodine determined by standard sodium thiosulphate. From these data are obtained the quantity of iodine consumed. This quantity of iodine, mulitiplied by the "ratio of alkaloid to 1 of iodine" gives the quantity of alkaloid sought. If preferred, but generally with less convenience to the chemist, the number of c.c. of decinormal solution of iodine consumed may be multiplied by the "alkaloidal factor of 1 c.c. N/10 I sol."

Verification of the Iodine Factors by Volumetric Control.

For Atropine.—In the following estimations of the strength of atropine solutions both the iodine solution and the sodium thiosulphate solution were strictly decinormal. Of the iodine solution 20 or 25 c.c. were put into a 100 c.c. measuring flask, and atropine solutions of known strength run in from a burette, and the operation continued as described above. When the supernatant liquid was perfectly transparent the flask was filled up to 100 c.c., and 50 c.c. were filtered off. In these 50 c.c. the excess was determined by means of the tenth normal thiosulphate solution, and the strength of the atropine solutions calculated by using the factor 0·0036048 for every c.c. of decinormal iodine used up.

	Actual strength. Per cent.	Number of c.c. of the atropine solution taken.	Number of c.c. of the tenth normal iodine used up.	Results in strength. Per cent.
1.	0·50	12	15·6	0·47
2.	0·40	15	14·9	0·36
3.	0·30	17	13·2	0·28
4.	0·25	12	10·0	0·28

For Strychnine.—To test the correctness of the ratio of 1 of free iodine to 0·4390 of strychnine, two solutions were prepared, one of 1 per cent, the other of 0·612 per cent of the alkaloid. The estimations, by the volumetric method, gave results as follows:—

	Actual strength. Per cent.	Strychnine solution taken. C.c.	Iodine consumed.	Results obtained. Per cent.
1.	1·0	3	0·07	1·026
2.	0·612	7	0·191	0·633

For Brucine.—Two solutions of the alkaloid were made, and estimated volumetrically, calculating by the ratio 1 part of iodine to 0·5179 part of anhydrous brucine, with these results:—

	Actual strength. Per cent.	Brucine solution taken. C.c.	Iodine consumed.	Results obtained. Per cent.
1.	1·0	10	0·193	0·999
2.	0·5	10	0·096	0·497

For Morphine.—Three standard solutions were made of strengths in anhydrous alkaloid as below tabulated. This was done by weighing a good article of well-crystallised morphine, free alkaloid, as $C_{17}H_{19}NO_3.H_2O$. The results were calculated by the ratio 1 of iodine to 0·74918 of morphine, absolute.

	Strength in per cent.	Morphine solution. C.c.	Iodine solution. C.c.	Iodine consumed.	Result in per cent.
1.	0·518	10	20	0·070116	0·525
2.	0·259	10	20	0·334272	0·257
3.	0·100	10	20	0·014023	0·105

The Iodine Factors of the Alkaloids so far Determined.

Higher periodide formed.	Ratio of alkaloid to one of iodine.	Alkaloid factor of 1 c.c. tenth-normal iodide solution.
Atropine, $C_{17}H_{23}NO_3.HI.I_8$ ..	0·2849	0·0036048
Strychnine, $C_{21}H_{22}N_2O_2.HI.I_6$	0·4390	0·00555467
Brucine, $C_{23}H_{26}N_2O_4.HI.I_6$ ..	0·5179	0·00655299
Morphine, $C_{17}H_{19}NO_3.HI.I_3$..	0·74918	0·00947937
Aconitine, $C_{33}H_{45}NO_{12}.HI.I_6$.	—	—
By Gomberg in 1896 (*Journ. Am. Chem. Soc.*, xviii., 339):		
Caffeine, $C_8H_{10}N_4O_2.HI.I_4$ ..	0·3834	0·00485

(To be continued).

CORRESPONDENCE.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

To the Editor of the Chemical News.

SIR,—I gather from Mr. F. W. Daw's article of last week that he considers the presence of carbon in the iron with which permanganate solutions are standardised to be an insufficient explanation of the low results obtained on using the permanganate to titrate manganous salts. At the same time I understand that Mr. Daw allows this to be a source of error when permanganate or even bichromate solutions are standardising by straightway titrating a solution of iron wire in dilute sulphuric or hydrochloric acid.

If the purity of the ferrous ammonium sulphate used, and particularly its freedom from carbonaceous matter, has been placed beyond doubt, then, of course, there must be some other reason for the low results.

Mr. Daw, I presume, is aware that the reaction between permanganate and manganous salts forms true MnO_2 as expressed by the equation only under certain conditions. The fact that he made no mention of such a possible source of error suggests that he thinks some other explanation is necessary. May I let the importance of the subject be my apology for troubling him to say whether he is able to explain the apparent anomaly?

I notice that in analysing the standard ferro-manganese the Mn_3O_4 precipitate is heated in a platinum crucible over a blast lamp. As platinum at high temperatures is permeable to gases, and as some of the gases of the flame may exert a reducing action, is not this procedure questionable in so delicate a matter?—I am, &c.,

HARRY BREARLEY.

Totley, near Sheffield.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 23, December 5, 1898.

Action of Acetylene on the Ammonium Compounds of the Alkalis.—Henri Moissan.—The author has obtained the following acetylene acetylides by acting on the ammonium compounds of the alkaline metals with acetylene:—$C_2K_2.C_2H_2$, $C_2Na_2.C_2H_2$, $C_2Li_2C_2H_2.2NH_3$, $C_2Ca.C_2H_2.4NH_3$. All these compounds dissociate and leave the carbides or the corresponding acetylides, C_2K_2, C_2Na_2, C_2Li_2, C_2Ca. When the ammonia compounds are acted on by acetylene, hydrogenation of the acetylene takes place, and ethylene is produced. The acetylene compounds of the carbides are soluble in ammonia, and this property causes different reactions to take place at a low temperature.

Colour of Calcium Carbide.—Henri Moissan.—The author has conducted a series of experiments to discover whether the reddish brown appearance of the crystals of calcium carbide is due to an impurity or is a property of the salt itself. He finds that when the carbide is absolutely pure, it is quite transparent and colourless, but the merest trace of iron gives it the reddish brown appearance.

The Properties of Aluminium.—A. Ditte.—For some time aluminium has been considered to be a metal which resisted the greater number of chemical reagents. The author's experiments show that this is not the case. When the metal is placed in dilute acid it dissolves rapidly at first, but a layer of gas is deposited on the surface which resists further action. This layer is found to adhere very firmly to the metal. By getting rid of the gas as fast as it is formed, either by working at reduced pressure or by some other means, it is found that the metal dissolves away entirely. In the case of a solution of common salt, the following reaction takes place:—$Al_2+6NaCl+3H_2O=Al_2Cl_2+3Na_2O+3H_2+157{\cdot}3$ cals.; but a double decomposition follows,—

$$Al_2Cl_6+3Na_2O=Al_2O_3+6NaCl+287 \text{ cals.},$$

and the deposit of the layer of Al_2O_3 arrests further action. The same reaction occurs when a plate of aluminium is placed in a solution of a salt of the alkaline earths. In fact, the author's experiments tend to show that aluminium is attacked in a more or less marked manner by all chemical agents.

Displacement of Metals by Hydrogen.—Albert Colson.—The results which have been proved concerning the action of bases or of free acids on dry salts apply to the reciprocal displacements of the metals. For example, hydrogen, considered as a volatile metal, displaces silver and copper from their dry salts. This reaction should be reversible, since the substitution of the metals by hydrogen is endothermic; but it is not so, owing to the fact that the absorption of hydrogen increases with the temperature. The author has experimented on the displacement of silver by hydrogen in various salts under varying physical conditions.

Synthesis of Phenol by Acetylene.—M. Berthelot.—The author has effected many syntheses by means of acetylene, one of the most interesting being that of phenol, which is obtained either through the condensation of acetylene in benzine, or by the action of potash on a sulphonated derivative of acetylene. In both cases the synthesis only requires a temperature of about 200°.

No. 24, December 12, 1898.

The Mixed Phosphates of Ethyl and Phenyl.—Albert Morel.—The author has investigated the action of the di- or monochlor-alcoholic phosphates on phenols or phenolates of the alkalis, and has found that they produced mixed phosphoric ethers, identical with those formed by the action of triphenyl phosphate on alcoholates of the alkalis. The ethers selected were—

$PO\begin{cases}OC_6H_5\\OC_6H_6\\OC_2H_5\end{cases}$ and $PO\begin{cases}OC_6H_5\\OC_2H_5\\OC_2H_5\end{cases}$.

Details of their preparation and properties are given.

Transformation of the Carbonate of Orthocresol into a Homologue of the Phthalein of Orthocresol.—P. Cazeneuve.—The carbonate of orthocresol mixed with excess of soda-lime undergoes an interesting molecular transformation, resembling that of phenyl carbonate and sodium into sodium salicylate. The author gives the method of preparation of the new compound expressed by the following equations;—

(i.) $2CO<\begin{matrix}OC_6H_4CH_3\\OC_6H_4CH_3\end{matrix}+2NaOH+O=$

$$=\begin{matrix}CO.OH\\CH_2\end{matrix}>C_6H_3.CH<\begin{matrix}C_6H_3<\begin{matrix}OH\\CH_3\end{matrix}\\C_6H_3<\begin{matrix}OH\\CH_3\end{matrix}\end{matrix}+$$

$$+Na_2CO_3+H_2O+C_6H_5OH;$$

(ii.) $$\begin{matrix}CO.OH\\CH_2\end{matrix}>C_6H_3.CH<\begin{matrix}C_6H_3<\begin{matrix}OH\\CH_3\end{matrix}\\C_6H_3<\begin{matrix}OH\\CH_3\end{matrix}\end{matrix}+O=$$

$$=C<\begin{matrix}C_6H_3<\begin{matrix}OH\\CH_3\end{matrix}\\C_6H_3<\begin{matrix}OH\\CH_3\end{matrix}\\C_6H_3<\begin{matrix}CH_3\\O\end{matrix}>CO\end{matrix}+H_2O.$$

This molecular transformation is not observable in the cases of the carbonates of meta- and para cresol.

Chlorination of Benzene in presence of Aluminium Chloride.—A. Mouneyrat and Ch. Pouret.—In a previous paper the powerful chlorinating action of $AlCl_3$, in the case of the members of the fatty series, was demonstrated. In the present article the application of the same reaction to hydrocarbons of the aromatic series is discussed. The results are similar in both cases. The aluminium chloride forms a chlorine carrier as efficient as iodine, and has the advantage of producing no by-products. The typical reaction is expressed as follows:—

1. $C_6H_6+AlCl_3=C_6H_5-AlCl_2+HCl.$
2. $C_6H_5-AlCl_2+Cl_2=C_6H_5Cl+AlCl_3.$

Action of Oxidising Agents on certain Nitrogen Compounds. — Œchsner de Coninck. — The oxidising agents employed were chromic acid and potassium bichromate; and the oxidation of substances such as hydroxylamine, phenylhydrazine, guanidine, hydrazine, methane, acetamide, benzamide, urea, and ammonia compounds, was examined.

MISCELLANEOUS.

Institute of Chemistry. — January Examinations, 1899.—*Names of Candidates who Passed the Practical Examination for the Associateship:* Arthur Jenner Chapman, Ferdinand Edward Paul Forster, George Percy Lishman, B.Sc. (Edin.). *Intermediate Examination:* Stafford Aston, Walter Lionel Blackman, Basil Radcliffe Coysh, Henry Dixon Hewitt, Alfred Hill, Henry Wulff Kinnersley, John Rogers, Frank Shedden, B.Sc. (Lond.), Leonard Victor Wright, B.A. (Cantab.). *Final Examination for the Associateship.* — In Branch "A" (Mineral Chemistry): *John Golding, *Walter Charles Hancock, B.A. (Cantab.), Arthur Marshall, A.C.G.I. In Branch "B" (Metallurgical Chemistry): John Imrie, Roland Cecil Wild. In Branch "D" (Organic Chemistry: William Setten Gilles, A.C.G.I., Percy John Hinks, A.R.C.Sc. (Lond.), Thomas Goode Joyce, B.Sc. (Lond.). In Branch "E" (The Analysis of Food and Drugs, and of Water): *John Francis Hutchins Gilbard, Charles Adolphus Hackman, Francis Samuel Young, M.A. (Oxon). (Those marked with an asterisk for the Fellowship).

The Separation of Mercury and Bismuth. — MM. Vanino and Treubert.—This method of separation is based on the complete precipitation of the mercuric chloride in the state of mercurous chloride, in dilute hydrochloric solution, by a mixture of peroxide of hydrogen and hypophosphorous acid. The bismuth remains in solution, and can be subsequently precipitated by a fresh addition of hypophosphorous acid. To the dilute hydrochloric solution of the salts of mercury and bismuth, we add an excess of a solution containing one drop of commercial hypophosphorous acid for each c.c. of peroxide of hydrogen. After standing for an hour the mercurous chloride is filtered off and quickly washed with dilute hydrochloric acid, then with distilled water, after which it is dried at 105° C. The filtrate is heated and made slightly alkaline with caustic soda. We then add the hypophosphorous acid and heat the solution while constantly stirring, until a black precipitate is formed and the liquid becomes clear. The bismuth is filtered off in a Gooch crucible, and washed first with water, then with alcohol, and dried at 105° C. —*Berichte.* xxxi. [2], p. 129.

NOTES AND QUERIES.

**** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Synthesis of Ethyl Alcohol.—(Reply to Frank Wood).—In reply to your enquiry (CHEM. NEWS, lxxviii., p. 305), you will find the original statement of Berthelot in the *Comptes Rendus*, l., p. 806, and liv., p. 515, that acetylene forms ethylene. The whole subject is discussed in "Die Metallcarbide und ihre Verwendung," von Professor Dr. Felix B. Ahrens, Stuttgart, 1896.—W. G. BROWN, Missouri State University, Columbia, Missouri, U.S.A.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Society of Arts, 8 (Cantor Lectures). "Bacterial Purification of Sewage," by Dr. Samuel Rideal.

TUESDAY, 31st.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

—— Society of Arts, 8. "The Centenary Exhibition of Lithography," by E. F. Strange.

WEDNESDAY, Feb. 1st.—Society of Arts, 8. "The Cost of Municipal Enterprise," by Dixon H Davies.

THURSDAY, 2nd.—Royal Institution, 3. "Tibet and the Tibetans," by A. Henry Savage Landor.

—— Chemical, 8. "Maltodextrin, its Oxidation Products and Constitution" and "On Attempts to prepare Pure Starch Derivatives through their Nitrates," by H. T. Brown, LL.D., F.R.S., and J. H. Millar. "An Isomeride of Amarine," by H. Lloyd Snape, D.Sc., Ph.D., and Arthur Brooke, Ph.D. "Propylbenzenesulphonic Acids," by G. T. Moody, D. Sc. "Derivatives of Dibenzylmesitylene," by W. H. Mills and T. H. Easterfield. "On the Action of Chlorosulphonic Acid on the Paraffins and other Hydrocarbons," by S. Young, D.Sc., F.R.S. "The Preparation and Properties of Nitrogen Iodide"; "The Action of Light upon Nitrogen Iodide"; "The Action of Alkaline Hydrates, of Water, and of Hydrogen Peroxide upon Nitrogen Iodide"; "Theory of the Formation and the Reactions of Nitrogen Iodide," by F. D. Chattaway, M.A., and K. J. P. Orton, M.A. "The Action of Reducing Agents on Nitrogen Iodide"; "The Action of Acids upon Nitrogen Iodide," by F. D. Chattaway, M.A., and H. P. Stevens, B.A. "The Composition of Nitrogen Iodide," by F. D. Chattaway, M.A.

FRIDAY, 3rd.—Royal Institution, 9. "The Roman Defences of South-East Britain," by Victor Horsley, M.B., B.Sc., &c.

SATURDAY, 4th.—Royal Institution, 3. "Brahms" (with Musical Illustrations), by Sir Alexander C. Mackenzie, Mus. Doc.

BERICHTE DER DEUTSCHEN GESELLSCHAFT Wanted, from 1868 to 1879 inclusive.—Address, F.W.R., 2, Farcliffe Place, Bradford.

Wanted, Chief Chemist and Manager of Works by a leading London firm of Manufacturing Chemists employing several hundred people. The qualifications necessary for the position are high and well grounded scientific knowledge and attainments, good practical experience in carrying out manufacturing processes, exceptional powers of organisation and administration, tact, good judgment, capability to direct and control scientific workers engaged in the manufacture of fine Medicinal Chemicals and Pharmaceutical Products. A gentleman with University Training and Degrees preferred. The position commands a liberal salary. Replies will be treated in the strictest confidence if so desired.—Address, stating age, qualifications, and experience, to "Manager," care of Messrs. Maikby, Stewart, and Co., 57, Coleman Street, London.

THE CHEMICAL NEWS.

VOL. LXXIX., No. 2045.

THE PREPARATION AND SOME OF THE PROPERTIES OF PURE ARGON.*

By WILLIAM RAMSAY, F.R.S., and MORRIS W. TRAVERS.

(Concluded from p. 39).

Density of Argon.

FOR a preliminary determination of the density of the various samples a bulb of about 33 c.c. capacity was employed. It is much easier to ensure the purity of a small sample of gas than of a large one; and it will be seen that very concordant determinations are obtainable with a small quantity. The limit of error is probably not greater than one part in a thousand. The results are expressed in terms of O = 16.

	Capacity of bulb. C.c.	Temp.	Pressure. M.m.	Weight. Grm.	Density.
1.	32·762	19·05°	535·1	0·03786	19·65
2.	,,	15·70	712·0	0·05265	19·95
3.	,,	17·00	662·2	0·05012	19·95
4.	,,	14·55	749·8	0·05460	19·91
5.	,,	15·60	740·4	0·05389	19·97
6.	,,	16·15	760·2	0·05501	19·95

The spectrum of No. 4, examined later, showed a trace of nitrogen; the density of No. 6 was confirmed by other two determinations, each made after further sparking.

No. 1 was the first portion boiled off, and therefore its density is lower than that of the other fractions, probably owing to its still containing some neon and helium. The rest of the samples have a constant density, approximately 19·95.

A larger quantity of No. 5 was then purified by long-continued sparking, and its density was determined in a bulb of greater capacity. To show the influence of such purification results are given, obtained before it was complete. The gas under such conditions showed a trace of the nitrogen spectrum. The portion last weighed was spectroscopically pure.

Capacity of bulb. C.c.	Temp.	Pressure.	Weight.	Density.
163·19	15·47°	767·1	0·27235	19·935
,,	16·97	764·8	0·26985	19·914
,,	13·34	742·8	0·26591	19·952
,,	12·95	741·3	0·26586	19·961

After the first of these determinations the gas was passed over a mixture of red-hot magnesium and lime, and subsequently over red-hot copper oxide, in order to remove hydrogen. But after determining the density, the gas was examined spectroscopically, and was found to contain hydrogen. The gas was therefore again sparked, when the density 19·952 was found. This specimen was also examined spectroscopically, and was found to be absolutely free from all visible traces of impurity. The last weighing refers to the same sample of gas, and was made as a control experiment.

These results conclusively prove that the density of argon, purified from its companions, does not differ greatly from that obtained by Lord Rayleigh, viz., 19·94, nor by one of us, viz., 19·941. The true density may, we think, be safely taken as the mean of the last two determinations, viz., 19·957.

* A Paper read before the Royal Society, December 15, 1898.

This corresponds with the mean of the four reliable determinations with the small bulb, viz., Nos. 2, 3, 5, and 6, which is 19·955.

Refractivity of Argon.

The refractivity of pure argon was next determined. The measurements were made according to the plan suggested by Lord Rayleigh (*Roy. Soc. Proc.*, vol. lix., p. 201). The samples investigated were Nos. 1, 2, 5, and 6. The comparison was made with air.

1. 0·9620 Contains neon and helium.
2. 0·9687
5. 0·9647. Mean, 0·9665.
6. 0·9660.

The refractivity of a previous sample of argon, obtained from the middle of the 15 litres, during the second liquefaction, was 0·9679, a number differing only slightly from that given above.

The refractivity of argon containing krypton, which had a density 20·01, was much higher than the number given above for pure argon, for it reached 1·030 as a mean of two determinations. Evidently then the body possessing the high refractivity was not present in No. 6 in greater proportion than in No. 2, otherwise the refractivity of No. 6 would have shown an increase over that of No. 2.

The refractivity of pure argon differs somewhat from the value for crude argon found by Lord Rayleigh, viz., 0·961 (*Roy. Soc. Proc.*, vol. lix., p. 205), and also from that previously found by ourselves, 0·9596. The removal of neon, which appears to have a very low refractivity, and of helium, of which the refractivity is 0·1238, accounts for the increased refractivity of a sample from which they are absent. The gases which we have recently found in air and in crude argon will form the subject of a future communication. Suffice it to say that the amount of neon and helium is much more considerable than that of the others, and that their effect on crude argon is, therefore, much more marked on its density and refractivity.

To revert to the opening sentences of this communication, we may point out that the remarks on the homogeneous nature of argon were just at the time. The change in its physical constants, caused by the mixture of more recently discovered gases which it has been shown to contain, is exceedingly small, and does not call for any serious alteration in the original paper on "Argon, a New Constituent of the Atmosphere."

The Density of Argon at the Boiling Point of Oxygen.

In an addendum to the original paper on Argon (*Phil. Trans.*, A, 1895, p. 239), the expansion of argon by rise of temperature to 250°, as well as its contraction by fall of temperature to −88°, was determined. There is a considerable difference between the temperature at which nitrous oxide boils and that at which oxygen boils, and it was thought worth while to ascertain whether argon behaves as a normal gas down to the boiling point of oxygen. Olszewski (*loc. cit.*, p. 257), gives the boiling point of argon as −187°, and that of oxygen as −182·7°; at the latter temperature, therefore, argon would not be far removed from its own condensing point. The interesting question, of course, is the possible polymerisation of argon at such a low temperature.

No sign of any polymerisation has been observed, as is shown by the following data:—

Hydrogen Thermometer.

Temperature. °C.	Pressure. m.m.	Volume.	R.
99·7	1091·5	1·0026	2·9362
0·0	803·2	1·0000	2·9121
−182·7	269·6	0·9953	2·9715

Argon Thermometer.

100·1	1414·9	1·0026	3·8095
0·0	1040·0	1·0000	3·8022
−182·7	353·2	0·9953	3·8930

No correction has been made for the unheated or uncooled stem of the thermometer; but it is obvious that although the lowest temperature lies close to the boiling of argon, the ratio of the values of PV/T of hydrogen and argon at that temperature, as well as the others, is practically constant.

ON THE

ESTIMATION OF CARBON AND HYDROGEN IN VOLATILE ORGANIC LIQUIDS.

By F. W. STREATFEILD, F.I.C., and LEWIS EYNON.

It is well known that, in the estimation of carbon and hydrogen in liquids that boil or vapourise at a low temperature, many practical difficulties are met with. When the substance contained in a glass bulb is manipulated within the combustion-tube very great care must be taken to prevent too rapid expulsion of the liquid from the bulb, otherwise failure results from incomplete combustion and backward diffusion. Again, when the substance is contained in a small sealed tube outside the combustion-tube, a great deal of experience and dexterity is required in breaking the ends of the tube and preventing loss.

Having occasion recently to undertake the estimation of the constituents of some volatile organic liquids, we have devised the following little apparatus, which, we believe, will greatly simplify operations of the kind here under consideration. Reference to Fig. 1 will, we hope, render the construction of the apparatus evident.

It consists of a moderately large test-tube, preferably made from thick glass tubing fitted with a caoutchouc stopper pierced with three holes. Through one of these a glass tube passes; this is connected with the air or oxygen supply, and just dips under the surface of some mercury placed in the tube. Another glass tube connects the apparatus with the combustion tube. The third hole carries a glass rod bent over or flattened at one end. The glass rod may be made to slide in a glass tube, supported and made air-tight by a piece of well-fitting caoutchouc tubing, as shown in the sketch.

The method of using the apparatus requires little or no explanation. The substance, contained in a sealed thin glass bulb, is placed in the test-tube, the stopper inserted, and the apparatus connected to the combustion-tube. Everything being in order, the glass tube is broken by pressing down the rod, and the vapour slowly and carefully expelled by the current of air or oxygen. Towards the end of the operation the apparatus may be surrounded with hot water contained in a beaker. It will be seen that, by means of the mercury trap, there is little or no possibility of the vapour of the substance diffusing backwards, and if the current of air be carefully regulated complete combustion results, provided, of course, there is a good length of copper oxide in the combustion-tube.

In cases where, owing to the nature of the vapour, the caoutchouc fittings may be attacked, we propose the following modification (see Fig. 2): it consists, as will be seen, in simply inverting the test-tube and bending the air-supply tube over on itself, so that the end of the tube dips under the surface of the mercury which covers the caoutchouc stopper.

Of course a more elaborate apparatus might be constructed by fusing the entrance and exit tubes into the sides of the test-tubes.

We append the following results obtained with the apparatus in the combustion of petroleum ether:—

	Carbon.	Hydrogen.	Total.
1.	83·57 per cent	16·44 per cent	100·01 per cent
2.	83·337 ,,	16·578 ,,	99·915 ,,

We regret that we are unable to publish further results as unfortunately our work has been interrupted. We

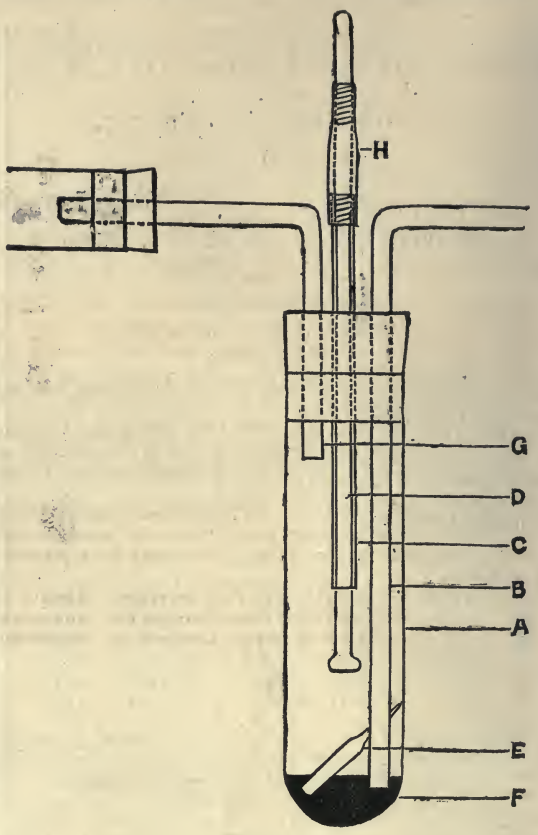


Fig. 1.

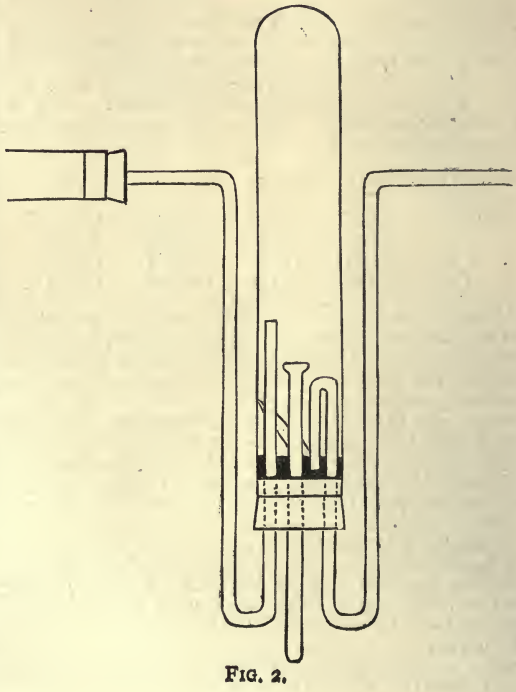


Fig. 2.

venture, however, to submit the foregoing, incomplete as it is, hoping it may be sufficiently interesting and suggestive to induce others to experiment with our apparatus.

City and Guilds Technical College,
Finsbury, E.C.

APPARATUS FOR THE SAPONIFICATION OF FATS, OILS, &c.

By J. G. ANNAN.

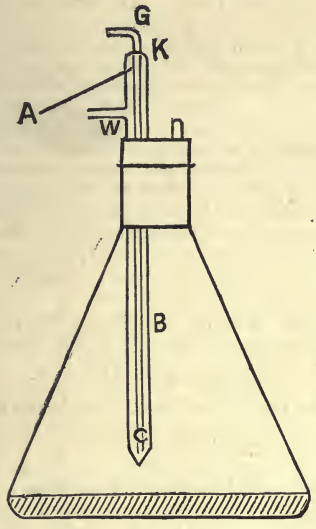
Having had a number of oils to examine lately, I devised the following convenient arrangement for carrying out the preliminary saponification necessary in some of the determinations:—

A small condenser is made according to figure A of accompanying sketch.

B is a tube of about $\frac{3}{8}$ths inch bore and about 5 inches long, with a side tube blown at W and a central tube of about $\frac{1}{4}$th inch bore C C jointed or passed through a cork at K.

An Erlenmeyer flask of any convenient size is taken and fitted with a cork perforated with two holes, one to carry the condenser, the other to be closed by a piece of glass rod.

Introduce the weighed fat and measured quantity of alcoholic potash, insert the cork carrying the condenser, but leave the small hole open. Connect the condenser



with the water supply and place the flask over a small flame. When, by gentle boiling, the air is considered to be displaced from the flask, insert the glass rod, and at the same time turn on the water.

The gas may now be turned up to boil the liquid vigorously, and the apparatus may be left without further attention until the saponification is considered to be complete, when the glass rod may be withdrawn and the gas turned out.

Amongst the first experiments made the end of a small manometer was inserted into the open hole instead of a glass rod, in order to observe variations in pressure. Through many considerable variations of flame the internal pressure remained practically the same as the atmospheric pressure.

It is evident that this apparatus has some advantages over that generally used for saponifications, more especially in the determination of Koettstorfer's figure.

CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.*

By A. B. PRESCOTT and H. M. GORDIN.

(Concluded from p. 47).

Application in Assay of Crude Medicinal Drugs.

We have made estimations of total alkaloids in nux vomica, and in belladonna, by the periodide volumetric method, after extraction of the alkaloid in several ways, and have obtained satisfactory results. We have work in hand by which we hope to reach more expeditious methods of extraction. Among the menstrua under experimentation are a saturated solution of gaseous ammonia in ether, a chloroformic solution of ammonia (suggested by Siedler and Thomas, *Ber. d. Pharm. Ges.*, 1898, 28), and similar agents.

A Volumetric Assay of Opium.

The morphine was estimated as periodide, after successive treatment with benzol, amyl alcohol or acetone, and lime-water.

This method proceeds upon the following plan:—The opium alkaloids are set free by action of ammonia with certain solvents. The free narcotine, papaverine, codeine, and thebaine are then removed by percolation with benzene, after which the morphine is taken out by percolation with acetone,† in which the morphine is sufficiently soluble. The acetone is then evaporated off, and the residue taken up with lime-water, which completely dissolves and purifies the morphine. It remains to filter the lime solution, acidulate it with hydrochloric acid, and estimate the morphine as periodide by titration as already detailed in this paper.

In the percolation of the opium with different solvents to separate the morphine, we depend upon two things, (1) the preparing of the opium powder by digestion with the ammonia and the solvents and then drying, and (2) an admixture with dry common salt in transferring to the percolator.

The Materials for the Assay.—Opium in fine powder (No. 60 or finer), 1 grm.; stronger ammonia water; alcohol, ether, chloroform, pure benzene (crystallised); acetone, boiling between 54° and 58° C., and about 200 c.c.; some good lime-water; ordinary common table salt, about 20 grms.; some diluted hydrochloric acid (10 per cent); decinormal solution of iodine with potassium iodide (Wagner's reagent), and sodium thiosulphate solution standardised with the solution of iodine.

Directions for the Assay.—Of the opium in fine powder one grm. is weighed into a small mortar or deep dish, such as can be well covered with admission of a small pestle.‡ A mixture is made of 5 c.c. of stronger ammonia water, 5 c.c. of alcohol, 20 c.c. of ether, and 10 c.c. of chloroform. The opium is rubbed up with 2 or 3 c.c. of this mixture, to make a uniform paste, using a pestle that can be left in the dish when it is covered. The covered dish is now put aside for about three hours, from time to time moving the dish gently; about 15 grms. of well dried and finely powdered common salt are now added and carefully mixed into the mass. Then the dish is left open in a warm place, of 30° to 35° C., for two or three hours, when it is placed in a desiccator containing sulphuric acid and a dish of paraffin, a vacuum desiccator being preferable, until the mixture is perfectly dry, as shown by the looseness of the powder under the motion of the pestle. If left over night it is sufficient. The entire contents of the dish are now transferred to a little

* *Journal of the American Chemical Society*, xx., No. 9, Sept., 1898.

† Instead of acetone there may be used pure amyl alcohol, boiling between 128° and 132° C., and leaving no residue upon evaporation below the boiling-point.

‡ A screw-top ointment jar of mortar-shaped bottom and four or six ounces capacity serves very well.

glass percolator of about $1\frac{3}{10}$ c.m. (one half inch) inner diameter, and 22 c.m. (9 inches length,* rubbing out the dish twice with a little more of the dried common salt. The mass is now percolated with the benzene, until the percolate is colourless, and until upon evaporating 1 or 2 drops of the percolate in a watch-glass, taking up the residue with 4 or 5 drops of acidulated water, and adding a drop or two of Wagner's reagent, no turbidity appears (removal of alkaloids other than morphine). A shallow dish is now set under the percolator, and pure acetone used to continue the percolation to complete exhaustion, as found by evaporating 10 drops of the percolate on a watch-glass, taking up the residue with 2 or 3 drops of acidulated water, and adding a drop or two of Wagner's reagent, when no turbidity at all should appear. Usually as much as 200 c.c. of acetone are required. The acetone is now evaporated, at a temperature not exceeding 45° C., to complete dryness. The residue when cool is rubbed up with good fresh lime-water, the solution poured without filtering into a graduated stoppered cylinder of 100 c.c., the dish washed four or five times with portions of lime-water, to fully clean the dish, when lime-water is added to make the volume 100 c.c. The cylinder is now securely stoppered and well shaken for half an hour. O. the mixture enough is now filtered into another graduated cylinder, with glass stopper, to make up a filtrate exactly 50 c.c. To this liquid is added diluted hydrochloric acid (10 per cent) to just perceptible acidulation, and the tenth-normal iodine solution is slowly run in from the burette while gently shaking the cylinder until precisely 25 c.c. have been added. Water is added to any convenient mark of the cylinder, which is then stoppered securely and shaken vigorously and continuously (for about twenty minutes) until, on standing a minute or two, the supernatant liquid (of a pronounced iodine-red colour)† is perfectly clear and transparent. The liquid is now filtered off so as to take just one-half the volume of the filtrate. In this half of the liquid the excess of iodine is titrated back with the tenth-normal sodium thiosulphate solution, using starch as an indicator. The number of c.c. of the thiosulphate solution multiplied by 2, is subtracted from 25, the number of c.c. of iodine solution used. The remainder is now multiplied by the factor 1·89586 (0·0094793 × 2 × 100), the product being the percentage of morphine in the powdered opium as weighed.

The precautions most essential are (1) that the opium residue before percolation be thoroughly dried, (2) that acetone should not contain anything distilling below 54° C., or above 58° C., and (3) that after the added excess of iodine the container be continuously shaken until the precipitate is so fully separated that the solution above it is clear. An automatic shaker is an aid in this assay. A second estimation can be made with the remaining part of the lime solution.

Without the use of lime-water in purification of the morphine of the residue, we find the colour of the resulting acidulous solution to be inconvenient in the titration, and find the percentage figure to be uniformly higher than when obtained after lime solution. The vessel is easily cleaned from adhering morphine periodide by the use of acetone.

Results of the Opium Assay by the Periodide Method.

We can give here the results of assays of but 3 samples of powdered opium, these coming from three different reputable houses. They were all marked, sample A to contain 14 per cent, samples B and C to contain the quantity required by the U. S. P. Three analyses of each sample were made, and to sample A the U. S. P. method was also applied, and was found to contain 14·4 per cent morphine by that method. The volumetric method was carried out exactly as described above.

	Opium taken in grms.	Iodine consumed by one-half.	Percentage morphine found.
Sample A.			
1	1·0036	0·116644	17·41
2	1·008	0·116732	17·37
3	1·0022	0·116642	17·44
Sample B.			
1	1·0033	0·08872	13·25
2	1·0023	0·08872	13·20
3	1·0026	0·08872	13·21
Sample C.			
1	0·9969	0·096319	14·48
2	1·0016	0·097219	14·55
3	0·9988	0·094552	14·19

As a Valuation of the Morphine of any Pharmacopœial Assay.

If it should be desired to estimate the alkaloid in the crystals obtained in assay by the pharmacopœia of this or any other country, the periodide volumetric analysis could be well applied as follows:—

Let the crude morphine obtained by the pharmacopœial method be taken up with lime-water, the latter made up to a given volume, and a measured portion of the filtered solution, placed in a graduated vessel and acidulated with hydrochloric acid; let a definite excess of the decinormal iodine be added, in small portions at a time, and shaken after each addition, till the periodide separates out, and the clear liquid retains a dark red colour, making up the mixture to a given volume; filtering off half and then titrating the excess of iodine in this half by standard sodium thiosulphate, the amount of iodine consumed can be easily found. Working on 10 grms. opium, a tenth portion of the lime-water solution would represent 1 grm. of opium, and the percentage of morphine would be equal to the weight of iodine consumed, multiplied by 74·918, or to the number of c.c. of the tenth-normal iodine consumed, multiplied by 0·94793. Several analyses could be made with the remaining part of the lime-water solution.

* The tube of a one-ounce syringe does very well.

† If the liquid does not have this red colour, it must be because of a lack of the indispensable excess of the iodine, of which an additional quantity should be added.

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 43).

Hypothetical Explanation.

THE facts are now perfectly clear, and it remains only to account for them by means of a plausible theory. In the first place, there can be no question that the gases proceed from a residue of basic nitrate imprisoned in the oxides in question; the fact that oxides prepared from the carbonates contain little or no gas would alone be sufficient support for this point of view. The first matter to be considered is, then, the dissociation of this residual nitrate, which is probably wholly analogous to that of calcic carbonate as studied by Le Chatelier (*Compt. Rend.*, 1886, cii., 1243; Nernst, *Theoret. Chem.*, 1894, p. 377). We may express this reaction, perhaps, in the following fashion, which indicates that the proceeding is supposed to take place in the gaseous phase, while the solids enter into the reaction solely by their vapour tension.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 22; also *American Chemical Journal*, November, 1898.

$$\underset{\text{Vapour.}}{Cu(NO_3)_2{\cdot}3CuO} \rightleftharpoons \underset{\text{Vapour.}}{4CuO} + [N_2O_5]$$

$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$

$$\underset{\text{Solid.}}{Cu(NO_3)_2{\cdot}3CuO} \qquad \underset{\text{Solid.}}{4CuO}$$

It is probable that Graham's basic cupric nitrate $Cu(NO_3)_2{\cdot}3Cu(OH)_2$ is dehydrated before the nitric acid begins to leave; if it is not, of course 3 molecules of water must be added to the products above. The addition of the water does not affect the essential point in the following logic, however. The gaseous products of this reaction attain a pressure of 760 m.m. at about 280°.

The reaction represented above is evidently only a preliminary stage of the whole change; it may have scarcely begun, or may have run almost to an end in some cases before the dissociation of the nitric anhydride begins to enter into the problem. This dissociation may be complete, resulting in a mixture of the elementary gases, or it may (and does at ordinary pressures) stop at one of the lower oxides of nitrogen. Since the gases, whatever they may be, are necessarily held in microscopic cells, while their own volume under ordinary pressure is several times that of the total volume of the solid containing them, it is obvious that the pressure under which they exist must be very great. At this great pressure the stability of N_2O_5 must be very considerably increased, for the reaction $2N_2O_5 = 2N_2 + 5O_2$ is one which pressure must seriously affect, because of the change of volume concerned in it; but more probably the peroxide of nitrogen may be the first product of the reaction. In any event, it is evident that the complete separation of the oxygen and nitrogen does not take place immediately, for much less nitrogen was yielded by the specimens of each oxide heated for a short time at comparatively low temperatures than by like specimens heated longer or hotter.

Both of these reactions, the decomposition of the cupric nitrate as well as that of the oxides of nitrogen, evidently, then, require time for their completion, so that the maximum of gas contents is not immediately attained. Besides being accelerated by heat, they are also possibly both hastened by the escape of a portion of the oxygen, an interesting phenomenon which occurs side by side with the decomposition. To make the matter clearer, let us represent the dissociation of the oxide of nitrogen by the general formula $2NO_x = N_2 + xO_2$. The speed of this reaction is represented by the equation—

$$-\frac{dc}{dt} = k c^2 - k^1 c_1 c_2^x,$$

an expression which increases in magnitude as c_2 (the concentration of the oxygen) diminishes. Since it is probable that k^1 is very small,—that the chief tendency of the reaction is from left to right,—this cause of acceleration is not an important one. In a similar way the decomposition of the oxides of nitrogen likewise accelerates the more complex reaction into which the solids enter.

In every case this decomposition of the oxides of nitrogen, and therefore that of the cupric nitrate, had nearly advanced to completion before the oxygen had all been expelled. This led to the existence of a maximum of gas volume after a brief heating, a maximum less marked in the case of cupric oxide than in the other cases, because the extra oxygen escapes from cupric oxide almost as fast as it is formed. Thus many of the apparent eccentricities in the behaviour of the gases find a simple and adequate explanation. The numerous results with different oxides were sought in the hope that the relations might be capable of quantitative proof according to the law of mass action, as well as of qualitative demonstration, but the great number of possible compounds and reactions made this hope vain.

It remains only to devise an hypothesis to explain perhaps the most interesting phenomenon under discussion, to show why the oxygen is capable of escaping more rapidly than the nitrogen. Obviously diffusion or transpiration cannot account for this; for any orifice, no matter how small, which would allow the oxygen to escape, must also allow the nitrogen to escape. The only possible explanation is the supposition that the oxygen finds its way out chemically, by uniting with metal or a lower oxide which has momentarily released some of its proper supply of oxygen. The displaced gas, being forced to find another berth, presently in its turn occupies the place of still another portion, and so on, until most or all of the excess has found its way out of prison. Of course the nitrogen cannot use this means of escape, for it is not surrounded by a compound which yields it upon dissociation; the nitrogen can only escape through holes originally present or formed by the re-arrangement of the substance of the solid.

This hypothesis suggests Grotthus's obsolete explanation of electrolysis, or rather that of Clausius; for the most plausible conception is that in the hot rapidly-vibrating solid a portion of the oxygen which ought to be combined with the metal is always in a free state, and that this condition, by a recurring process of dissociation and association, permits relieving the high pressuure of the oxygen in the cell. It is possible that water occluded in the oxide may play the part of a go-between, but there is no experimental evidence of this. It is no new idea to explain the diffusion of hydrogen through palladium, or of carbon through iron in the cementation process, and other similar phenomena, by a similar mechanical conception.

Quite in accord with this point of view are a number of facts. In the first place cupric oxide, the most easily reducible of the oxides investigated, parts with its occluded oxygen with the greatest ease, at the same time obstinately retaining the nitrogen. The progressive increase in the tendency to retain oxygen in the cases of zinc and magnesium corresponds to the increase in the difficulty of reducing these oxides. In other words, the least stable oxide is the one which has the feeblest hold upon the occluded oxygen. Cupric oxide begins to lose this impurity with great rapidity at 520°, zincic oxide loses it less rapidly even at 750°, and magnesic oxide is still more obstinate. It is probable, moreover, that in the cases of zinc and magnesium there is a slight amount of transpiration, for a small part of the nitrogen was found to leave at the higher temperatures. This transpiration ought to assist the oxygen also to escape, although in somewhat less measure than the nitrogen; but in spite of this possibility of more rapid escape, the oxygen is still held more firmly than in the case of cupric oxide. In this latter substance all the *nitrogen* is retained indefinitely at temperatures below 850°, forming the constant gas residue noted in the first experiments; only when the definite structure of the oxide is broken up, and the dissociation tension of the cupric oxide becomes so great that cuprous oxide begins to be formed, does the nitrogen take its flight. On the other hand, a reducing atmosphere is needed to force zincic oxide to relinquish all its gas, unless an excessively high temperature is employed. Forty-three years ago Sainte-Claire Deville and Rivot showed that at a red heat such an equilibrium exists between zincic oxide, zinc, hydrogen, and water, as to enable zinc oxide to be sublimed in a current of hydrogen, the dissociated oxide re-forming when cooled (*Am. Chem. Phys.*, [3], xliii., 7, 477). This reaction undoubtedly enables the occluded gas to escape, by destroying the structure of the solid when gases from the flame are present.

Again, the fact that many solids, the oxides in question among them, manifest upon heating the peculiar contraction called "sintering," is evidence of the existence of molecular instability and possibility of re-arrangement. The hypothesis of partial dissociation at high temperatures is adequate to explain this.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 19th, 1899.

Professor DEWAR, F.R.S., President, in the Chair.

MESSRS. W. Ackroyd, E. M. Rich, and C. W. T. Woods were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Alfred Bolam, 31, Oxford Street, Newcastle-on-Tyne; James Washington Epps, 95, Upper Tulse Hill, S.W.; Ernest Barratt Fairweather, King's College Hospital, Lincoln's Inn Fields, W.C.; Colin Charlwood Frye, Burwood, Woodville Road, Ealing, W.; Edmund Vivian Gabriel, Bengal United Service Club, Calcutta; Harold Brewer Hartley, Romney Lodge, New Park Road, Clapham Park, S.W.; Tom Lacey Hewitt, Beech Field, St. John's, Higher Broughton, Manchester; Edward Flaxman Linstead, 35, Hayter Road, Brixton Hill, S.W.; Thomas Mackenzie, 8, Gardner Street, Glasgow; Joshua Maudsley, Merchiston Castle, Edinburgh; Arthur Mirrlees, Redlands, Kelvinside, Glasgow; Bernhard Mohr, 69A, Parliament Hill, Hampstead, N.W.; John Cavendish Molson, 42, Sackville Road, Hove, Brighton; John Trengove Nance, District Bank, Newcastle, Staffs.; William Walker Scott Nicholls, 230, Brockley Road, Brockley, S.E.; Horace Seymour Pyne, Castletown, Isle of Man; Arnold Stevenson, 4, Porchester Gardens, S.W.; Henry Fox White, Warnham, Woodland Road, Clifton, Bristol.

Of the following papers those marked * were read:—

*1. "*Researches on Moorland Waters. I. Acidity.*" By WILLIAM ACKROYD, F.I.C.

Moorland waters are consumed by over five and a quarter millions of people in England. The quality of acidity possessed by these waters, which has been associated with plumbo-solvent action, is therefore of great importance. The author differentiates between organic and inorganic acidity, and describes a method for ascertaining their amounts which consists of—(1) titration with N/100 alkali, using phenolphthalein as indicator, and (2) aspiration of air free from carbon dioxide through another portion, and a second titration for the residual acidity. The precautions to be used are described.

Data are given showing the loss of acidity due to diffusion in observations extending over 181 days. Comparisons are made proving that the differences in acidity of waters from various gathering grounds are due to differences of gradient. It is finally shown that the organic acid in solution, always assumed to be humic acid, is of lower equivalent than that of the lowest humic acid known.

DISCUSSION.

The PRESIDENT said that the plumbo-solvent action of the water supplied to Sheffield, Bradford, and Huddersfield, has been overcome by the addition of finely precipitated carbonate of lime in the reservoirs, with the result that the quality of the water was improved, not only by removal of the acidity, but also indirectly by precipitation of the dissolved peaty matter.

*2. "*Esterification Constants of Substituted Acetic Acids.*" By JOHN J. SUDBOROUGH and LORENZO L. LLOYD.

Goldschmidt has shown (*Ber.*, 1895, xxviii., 3218) that the esterification of an organic acid in the presence of a catalytic agent, such as hydrogen chloride and of a considerable excess of alcohol, may be regarded as a monomolecular reaction, and may, therefore, be represented by the equation—

$$\frac{dx}{dt} = K(a-x),$$

which, on integration, gives—

$$K = \frac{1}{t} \log_e \frac{a}{a-x};$$

where a is the initial concentration of the acid, $a-x$ the concentration of the acid after time t, and K the esterification constant. According to Goldschmidt, and also according to experiments made by the authors, K is directly proportional to the amount of hydrogen chloride present when dilute solutions are employed. In all cases K is calculated for normal hydrogen chloride.

The authors suggest that the letter E be used for the esterification constant, as K is already employed to denote the dissociation constant of an acid. E would then represent the esterification constant of an acid when normal hydrogen chloride is used, and E 10°/EtOH would represent the esterification constant of an acid with ethylic alcohol and a normal solution of hydrogen chloride at a temperature of 10°.

In the authors' experiments, N/40 hydrogen chloride was employed, and the organic acid was practically N/10 in all cases. Equal volumes of N/5 solutions of the acid in 100 per cent ethylic alcohol, and of N/20 hydrogen chloride in 100 per cent alcohol, were mixed, and 30 c.c. of the mixture run into small stoppered bottles, and maintained at a temperature of 14·5°. The contents of these bottles were then titrated with N/10, and finally with N/20 alkali, phenolphthalein being employed as indicator. The constants were calculated from the equation, and the results are given in the following table, together with the dissociation constants where known.

Acid.	Formula.	E 14·5°/EtOH.	K.
Acetic	$CH_3 \cdot CO_2H$	3·661	0·00180
Propionic	$CH_2Me \cdot CO_2H$	3·049	0·00134
Chloracetic ..	$CH_2Cl \cdot CO_2H$	2·432	0·155
Phenylacetic ..	$CH_2Ph \cdot CO_2H$	2·068	
Bromacetic ..	$CH_2Br \cdot CO_2H$	1·994	0·138
Iodacetic	$CH_2I \cdot CO_2H$	1·713	0·075
Isobutyric	$CHMe_2 \cdot CO_2H$	1·0196	0·00144
Trimethylacetic .	$CMe_3 \cdot CO_2H$	0·0909	0·000978
Dichloracetic ..	$CHCl_2 \cdot CO_2H$	0·0640	5·14
Diphenylacetic ..	$CHPh_2 \cdot CO_2H$	0·05586	
Dibromacetic ..	$CHBr_2 \cdot CO_2H$	0·0510	
Trichloracetic ..	$CCl_3 \cdot CO_2H$	0·0372	121·0
α-Bromisobutyric .	$CMe_2Br \cdot CO_2H$	0·0356	
αα-Dibromopropionic	$CMeBr_2 \cdot CO_2H$	0·0242	3·3
Tribromacetic ..	$CBr_3 \cdot CO_2H$	0·01345	

It thus appears that the rate of esterification depends on the constitution of the acid rather than on its strength. The authors are engaged in determining the esterification constants of substituted acrylic acids, and hope to extend the work to other series.

*3. "*Diortho-substituted Benzoic Acids.* Part IV. *Formation of Salts from Diortho-substituted Benzoic Acids and different Organic Bases.*" By LORENZO L. LLOYD and JOHN J. SUDBOROUGH.

In continuation of their work on diortho-substituted benzoic acids (*Trans.*, 1895, lxvii., 588 and 601; 1897, lxxi., 229), the authors have attempted to prepare salts from 2 : 4 : 6-trinitrobenzoic, 2 : 4 : 6-tribromobenzoic, 2 : 4 : 6-tribromo-3-aminobenzoic, metanitrobenzoic, and benzoic acids, and the following bases:—Trimethylamine, tripropylamine, tribenzylamine, diethylaniline, aniline, metabromaniline, metanitraniline, 2 : 4 , and 2 : 6-dibromaniline, pseudocumidine, mesidine, diphenylamine, and α- and β-naphthylamines, with results which are described in the paper. The investigation was undertaken in order to determine whether the capacity to form salts is dependent on (1) the strength of the acid and of the base, or (2) the constitution of the acid and of the base, or on both of these.

It was thought probable that a tertiary base of high molecular weight might not be able to combine with a diortho-substituted acid, but the reverse has proved to be

the case. Bases such as tribenzylamine, metanitraniline, &c., which will not combine with benzoic acid, readily combine with such diortho-substituted derivatives as 2 : 4 : 6-trinitrobenzoic, 2 : 4 : 6-tribromobenzoic, and 2 : 4 : 6-tribromo-3-aminobenzoic acids. This behaviour can only be accounted for by the fact that these are much stronger acids than benzoic, and combination between substituted benzoic acids and different bases would, therefore, appear to depend entirely on the strength of acid and strength of base.

Combination could not be effected between benzoic acid and metabromaniline, diethylaniline, pseudocumidine, or tribenzylamine, between metanitrobenzoic acid and tribenzylamine, and between trinitrobenzoic or tribromaminobenzoic acids and 2 : 4- or 2 : 6-dibromaniline, or diphenylamine.

The salts of trinitrobenzoic acid have no well-defined melting-points; when heated, they become dark coloured, then melt and decompose, the temperature at which this occurs depending on the mode of heating. Most of the other salts have well-defined melting-points.

*4. "*α-Ketotetrahydronaphthalene.*" By F. Stanley Kipping, D.Sc., F.R.S., and Alfred Hill.

The reaction involved in the synthesis of *α*-hydrindone from phenylpropionic chloride by means of aluminium chloride (*Trans.*, 1894, lxv., 480) is probably capable of wide application, and the authors have commenced experiments recently with the object of studying its usefulness in various directions. It has been found that when phenylbutyric chloride is treated with aluminium chloride under suitable conditions, it is converted into α-ketotetrahydronaphthalene by intramolecular condensation,

$$C_6H_5\cdot CH_2\cdot CH_2\cdot CH_2\cdot COCl = C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ CO\cdot CH_2\end{matrix}> + HCl;$$

a reaction which is exactly analogous to that by which *α*-hydrindone is prepared.

α-Ketotetrahydronaphthalene is a colourless highly refractive liquid, having a slight odour faintly recalling that of both camphor and peppermint. The *semicarbazone*,—

$$C_{10}H_{10}{:}N\cdot NH\cdot CO\cdot NH_2,$$

crystallises from alcohol in yellow needles or prisms, melts and decomposes at 217—220°, and is sparingly soluble in cold alcohol; when heated with dilute hydrochloric acid, it is decomposed, the ketone being regenerated. The *phenylhydrazone*, $C_{10}H_{10}{:}N\cdot NHPh$, crystallises from methylic alcohol in massive transparent plates melting at 84—85°; it is readily soluble in most ordinary solvents and is very unstable in the air. The *parabromophenylhydrazone*, $C_{10}H_{10}{:}N\cdot NH\cdot C_6H_4Br$, separates from alcohol and other solvents in long colourless prisms and melts at 117—118°; it is more stable than the hydrazone, but, like the latter, is decomposed by hot hydrochloric acid, the product being probably analogous to that obtained from the hydrazone of *α* hydrindone in a similar manner. The *oxime*, $C_{10}H_{10}{:}N\cdot OH$, separates from cold methylic alcohol in very large well-defined rhomboidal crystals; it melts at 102·5—103·5°, and is readily soluble in most ordinary solvents, but insoluble, or nearly so, in water. When reduced with sodium amalgam in acetic acid solution, the oxime is converted into a base, which is doubtless identical with the tetrahydro-*α*-naphthylamine described by Bamberger and Bammann (*Ber.*, 1889, xxii., 951).

*5. "*A New Method for Preparing Unsymmetrical Dimethyl- and Trimethyl-succinic Acids.*" By William A. Bone.

When ethylic sodiomalonate or ethylic sodiomethylmalonate is treated with ethylic *α*-bromisobutyrate in alcoholic solution, a mixture of ethylic salts of tricarboxylic acids is obtained. This, on hydrolysis with concentrated hydrochloric acid, yields a mixture of isomeric methyl derivatives of succinic and glutaric acids, in which, however, the glutaric acid very largely preponderates, the yield of the isomeric succinic acid being very small,

This is due to the fact that, in presence of the strongly alkaline solution, the ethylic *α*-bromisobutyrate readily loses hydrogen bromide, forming ethylic methacrylate, which then condenses with the ethylic malonate, or ethylic methylmalonate, according to the equation—

$$(CO_2Et)_2CH_2 + CH_2{:}CMe\cdot CO_2Et = (CO_2Et)_2CH\cdot CH_2\cdot CHMe\cdot CO_2Et,$$

and the resulting ethereal salt, on hydrolysis with concentrated hydrochloric acid, yields a methyl derivative of glutaric acid.

The author has found that if the sodium derivative of ethylic cyanacetate, which is almost insoluble in alcohol, be heated with an alcoholic solution of ethylic *α*-bromisobutyrate, the latter apparently does not lose hydrogen bromide, forming ethylic methacrylate, but reacts quite normally with the ethylic sodiocyanacetate, according to the equation—

$$(CO_2Et)(CN)CHNa + BrCMe_2\cdot CO_2Et = (CO_2Et)(CN)CH\cdot CMe_2\cdot CO_2Et + NaBr,$$

and a very good yield of unsymmetrical ethylic dimethylcyanosuccinate is obtained. This, on hydrolysis with concentrated hydrochloric acid, yields practically the theoretical quantity of an acid melting at 139—140°, the composition and properties of which are identical with those of unsymmetrical dimethylsuccinnic acid.

Unsymmetrical ethylic dimethylcyanosuccinate contains a hydrogen atom replaceable by sodium. The sodium compound, which is soluble in alcohol, readily reacts with methylic iodide, yielding ethylic trimethylcyanosuccinate, and this, on hydrolysis with concentrated hydrochloric acid, is converted into trimethylsuccinic acid.

By means of these reactions, unsymmetrical di- and trimethylsuccinic acids can be readily prepared in quantity. It is probable, moreover, that any mono-, di , or tri-alkyl derivative of succinic acid may be prepared by starting with ethylic cyanacetate, and working on the lines indicated; the author is, therefore, making a special study of these reactions.

6. "*The Production of Optically Active Mono- and Di-alkyloxysuccinic Acids from Malic and Tartaric Acids.*" By Thomas Purdie, F.R.S., and William Pitkeathly, B.Sc.

In continuation of a previous research (*Trans.*, 1898, lxxiii., 287), the authors have made further observations on the production of the ethereal alkyloxysuccinates in the interaction of silver malate and alkyl iodides. Small quantities only of these compounds were formed in the cases examined. A similar abnormal reaction occurs between silver tartrate and isopropylic iodide, an active ethereal salt of di-isopropoxysuccinic acid being found in the product; other alkyl iodides no doubt act in the same manner, though probably to a smaller extent.

The alcoholic hydroxyl groups of ethylic malate and tartrate are readily and completely alkylated by ethylic iodide in the presence of silver oxide. Diethoxysuccinic acid obtained by this method is a crystalline, highly dextrorotatory compound. The observations made on the rotatory powers of this acid and its ethylic, barium, and sodium salts furnish an explanation of the apparently anomalous results obtained by Rodger and Brame in preparing the alkylic tartrates from the silver salt (*Trans.*, 1898, lxxiii., 301).

The method of alkylation by means of alkyl iodides and silver oxide, which does not appear to have been used previously, is generally applicable to the ethereal salts of hydroxy-acids, and probably also to other substances of a similar nature. As racemisation does not occur in the process, it is specially adapted for the preparation of optically active compounds.

7. "*The Action of Ammonia on Ethereal Salts of Organic Acids.*" By Siegfried Ruhemann.

This paper is a continuation of the author's researches on the formation of pyridine derivatives from unsaturated

acids. The ethylic salts of these acids have been prepared by the interaction of sodium ethoxide with a mixture of the salts of the acids of the malonic series and those containing an acetylene linkage. Ethylic phenylpropenetricarboxylate, on treatment with ammonia is converted into *ethylic γ-phenyl-αα'dihydroxy-β-carboxylate*, crystallising in colourless prisms melting at 200°, and *phenyldihydroxypyridine*,—

$$CPh\begin{matrix}=CH\cdot C(OH)\\ =CH:C(OH)\end{matrix}\!\!>N,$$

melting at 254—255°. Ethylic phenylbenzylglutaconate, has been prepared from the product of the interaction of ethylic benzylmalonate and ethylic phenylpropiolate; on treatment with ammonia, it yields *γ-phenyl-β-benzyl-αα'-dihydroxypyridine* melting at 175°.

The author, further, gives an account of some experiments undertaken with the view of examining the action of ammonia on ethylic salts of saturated polycarboxylic acids. Ethylic propanetetracarboxylate is transformed into the diamido-imide of the acid (Ruhemann and Cunnington, *Trans.*, 1898, lxxiii., 1006), but its homologue, ethylic-β-methylpropanetetracarboxylate, forms the tetramide. Ethylic propanepentacarboxylate yields the triamido-imide of the acid,—

$$NH\begin{matrix}<CO-CH-CONH_2\\ \quad\quad\quad\quad|\\ <CO-CH-CH(CONH_2)_2\end{matrix},$$

melting at 212°, but ethylic phenylpropanetricarboxylate is transformed into the triamide melting at 230° with evolution of gas.

The author has also examined the action of sodium ethoxide on a mixture of ethylic phenylpropiolate with ethylic acetoacetate on the one hand, and with ethylic benzoylacetate on the other, and shows that the α-pyrone compounds, represented by the formulæ I. and II. are formed respectively.

$$CO_2Et\cdot C\begin{matrix}=CPh:CH\\ =CMe-O\end{matrix}\!\!>CO \qquad CO_2Et\cdot C\begin{matrix}=CPh:CH\cdot\\ =CPh-O\end{matrix}\!\!>CO$$

I. M.-p. 104°. II. M.-p. 120—121°.

The action of ammonia on the first of these compounds has been studied; it does not lead to the formation of a pyridine derivative, but yields the ammonium salt, $NH_2\cdot CMe:C(CO_2Et)\cdot CPh:CH\cdot CO_2NH_4$, which regenerates the pyrone compound on treatment with acids.

8. "*The Changes of Volume due to Dilution of Aqueous Solutions.*" By E. D. H. WADE, B.A.

In this paper, the contraction of solutions of different substances at various concentrations has been studied experimentally. Contraction is defined as the diminution of volume on mixing equal volumes of water and solution, stated for 100,000 c.c. of resulting solution; *e.g.*, if 50 c.c. of water + 50 c.c. of solution yield 99·999 c.c. of diluted solution, the contraction is said to be unity. Concentration is defined as the number of grm.-equivalents of substance in every 100,000 c.c. of the solution after dilution.

The author describes an apparatus for measuring such contractions directly to within about one-tenth of a unit without the need of determining the specific gravities of the experimental liquids. Observations were made on solutions of hydrogen, sodium, potassium, calcium, and strontium chlorides, potassium ferrocyanide, oxalic acid, cane-sugar, and urea. In almost all cases the equation—

$$X = \frac{n^b}{a}$$

was found to hold good in which X is contraction, n concentration, and a b are constant terms. In such cases, ϕ, the apparent volume of the substance, must be given by—

$$\phi = \text{const.} + \frac{n^b - 1}{a(2^b - 1)},$$

and values of ϕ thus calculated for various values of n are tabulated in the paper.

The first equation shows how X varies with the concentration. If the concentration be kept constant, and the dissolved substance varied, it is found that X increases regularly with the equivalent weight of the dissolved substance.

The apparatus described is available for many other cases where a change of volume follows a chemical process, as in the neutralisation of an acid.

9. "*The Thermal Effects of Dilution.*" By J. HOLMS POLLOK, B.Sc.

In thermo chemical determinations it is customary to operate with very dilute solutions to simplify the calculations connected therewith. To determine how far dilution might affect the thermal condition of salts in solution, a number of saturated solutions of salts were diluted with an equal bulk of water, and the following changes of temperature were noted:—

Saturated solutions at 9°.	Thermal change on dilution. 1st expt.	2nd expt.
NaCl	+0·50	+0·50
$NaNO_3$	−1·80	−1·85
Na_2SO_4	−0·05	−0·03
Na_2CO_3	−0·15	−0·20
KCl	−0·47	−0·47
KNO_3	−0·32	−0·38
K_2SO_4	−0·04	−0·03
K_2CO_3	−0·37	−0·44
NH_4Cl	−0·15	−0·13
$(NH_4)_2SO_4$	−0·43	−0·39
$CaCl_2$	+0·58	+0·62
$BaCl_2$	−0·07	−0·06
$MgSO_4$	+0·02	−0·01
$ZnSO_4$	+0·03	+0·05
$CuSO_4$	+0·02	+0·05
$FeSO_4$	+0·04	+0·00
$Pb(NO_3)_2$	−0·37	−0·33

The method employed was as follows:—Saturated solutions of the various salts were made, and half a litre of each placed in glass bottles of that capacity; an equal number of bottles were filled with half a litre each of distilled water, then all were placed in a large, shallow, wooden tub, in a room of uniform temperature, and left for twenty-four hours. A number of thin glass beakers of about a litre capacity, with glass stirring-rods shaped into a ring at the end, were provided, also a mercury thermometer graduated into tenths of a degree, and reading easily to a quarter of each division, as well as a differential alcohol thermometer with only about 4° on the whole stem, and the graduations of which corresponded to less than 0·01°. The temperatures of the bottles were taken as the experiments were made, and were found to be almost exactly 9°, though the different bottles did in point of fact vary as much as 0·05°, for which a proper correction was made. A bottle of solution and a bottle of water were then lifted out of the bath by a piece of flannel and poured simultaneously into a beaker standing on a thick piece of flannel, stirred up, and the temperature noted by both thermometers.

10. "*Halogen Derivatives of Acetonedicarboxylic Acid.*" Part I. By FREDERICK W. DOOTSON, M.A.

This communication is a preliminary note of an investigation of the action of halogens on ethylic acetonedicarboxylate. By the action of dry chlorine, *ethylic tetrachloracetonedicarboxylate* has been obtained. This substance, after purification, is a colourless, crystalline compound which melts at 30—30·5°, and decomposes on hydrolysis with aqueous soda or potash. It reacts with alcoholic potash, forming dichloromalonic and dichloracetic acids, and with ammonia yielding the amides of these acids. The action of bromine is very similar to that of chlorine.

11. "*The Detection and Determination of Sucrose in the presence of Lactose.*" By EDWIN DOWZARD.

The method proposed by the author is based on the

fact that sucrose is inverted by citric acid, whilst lactose is unaffected. The rotatory power of a solution of lactose is determined before and after treatment with citric acid. If the lactose is pure the rotation remains unchanged, but if sucrose is present it is considerably decreased. The amount of sucrose is readily calculated from the decrease in rotation.

12. "*Note on the Interaction of Formaldehyde with β-Naphthylamine Derivatives.*" By G. T. Morgan, B.Sc.

With a view of explaining the interactions which occur between formaldehyde and β naphthylamine (*Trans.*, 1898, lxxiii., 536), the author has investigated the action of this reagent on alkyl, benzyl, and halogen derivatives of the base.

Dibenzyl β-naphthylamine, $C_{10}H_7N(CH_2Ph)_2$, crystallises from alcohol in colourless leaflets, and from ethylic acetate in clusters of hard transparent prisms; it melts at 119—120°.

One compound only results when formaldehyde reacts with dialkyl- and dibenzyl-β-naphthylamine, two molecular proportions of the base condensing with one of the aldehyde to form a dinaphthylmethane derivative. The following compounds have been obtained: *tetramethyl-ββ8-diaminodinaphthylmethane*, $CH_2(C_{10}H_6NMe_2)_2$, which crystallises in transparent colourless prisms melting at 144°, the *tetrethyl* derivative, $CH_2(C_{10}H_6NEt_2)_2$, which crystallises in large colourless prisms and melts at 114°, and the *tetrabenzyl* derivative, $CH_2[C_{10}H_6N\cdot(CH_2Ph)_2]_2$, which forms lustrous leaflets melting at 164°.

The formation of these derivatives seems to be due to substitution in the contiguous α-position, as compounds of a different type are formed with methylene in the side chain when a halogen atom occupies this α-position.

Methylene 1-bromo-2-naphthylamine, $C_{10}H_6BrN{:}CH_2$, is obtained when 1-bromo-2-naphthylamine is treated with formaldehyde in acetic acid or in alcoholic solution; it crystallises from benzene or chloroform in colourless needles, and melts, with decomposition, at 144—145°. The corresponding *chloro*-derivative, $C_{10}H_6Cl\cdot N{:}CH_2$, obtained from 1-chloro-2-naphthylamine crystallises in colourless needles and melts at 179—180°. Both substances are compounds of the anhydroform-aldehyde type, and are converted into their generators on hydrolysis with acids, whilst the dinaphthylmethane bases are not altered under these conditions.

The investigation is being extended to other derivatives of β-naphthylamine.

PHYSICAL SOCIETY.

Ordinary Meeting, January 27th, 1899.

Mr. G. Griffith, M.A., Vice-President, in the Chair.

A mathematical paper was read by Dr. E. H. Barton, on "*The Equivalent Resistance and Inductance of a Wire to an Oscillatory Discharge.*"

Maxwell's treatment of the self-induction of cylindrical conductors was extended by Lord Rayleigh, in an article published in the *Phil. Mag.* for May, 1886, to alternate currents that follow the harmonic law at constant amplitude. Dr. Barton now modifies the analysis, and further extends it to include the decaying periodic currents obtained in discharging a condenser, and to the case of damped trains of high frequency, *i.e.*, to Hertz waves in general. The theoretical value (R″/R′) for the ratio of equivalent resistances to waves, respectively with and without damping, agrees very well with Dr. Barton's experimental results.

Mr. Oliver Heaviside, in a communication (here abstracted) said that he had, by another method of mathematical analysis, arrived at the same value as Dr. Barton for (R″/R′). In addition to the causes hitherto suggested as affecting the attenuation factor, it was possible that the conductivity of the wires to vibrations millions per second might be less than with steady currents, and that the voltage at the beginning of the wave-train might be large enough to cause some leakage. Both resistance and inductance become infinite with infinite damping, and they differ somewhat from the corresponding quantities for undamped waves.

Mr. Rollo Appleyard then described (1) some Experiments upon Dephlegmators, in which he has attempted to replace the platinum-gauze valves of the ordinary fractionating-tubes by bends in the tubes. The general form of the apparatus consists in a series of elongated bulbs, the top of each being connected to the bottom of the one above it by a horizontal S-shaped tube. The vapour condensed in any intermediate bulb falls back into the preceding S-bend. The first portions of the distillate are thus returned to the boilng-flask, leaving a little at each bend to act as a wash for the ascending vapour. At the early stage of distillation the bulbs and bends behave as required, but it is found that at the later stages certain of the bulbs become completely filled with liquid sustained by the upward pressure of the vapour, and, unless the heating is very carefully managed, "geyser" actions may take place. Some arrangement of overflow tubes is therefore required for the bulbs.

Mr. Appleyard also exhibited (2) a Temperature Tell-tale, to be used in connection with vats, and for other purposes where an alarm is to be sounded by making electric contact when temperature rises or falls beyond certain limits. A J-shaped glass tube has its short limb sealed and its long limb open. Water or other suitable liquid is poured in, completely filling the short limb. Mercury is then made to displace nearly all the water in the short limb; the surplus water in the long limb is removed by a pipette, and the mercury is adjusted to a convenient level. Two platinnm contact-wires are sealed into the glass at a short distance above the free surface of mercury in the long limb. The tube may be half an inch in diameter, with a long limb of 5 inches and a short limb of 2½ inches. The quantity of mercury in the tube is generally arranged so that, at temperatures below the boiling-point of the contained liquid, the mercury level is lowest in the long limb. In this case, if the temperature is raised to the boiling-point of the contained liquid, the mercury assumes approximately a common level in both limbs, for at the boiling-point of the liquid, under these conditions, the vapour-pressure is equal to the barometric pressure. Hence the liquid and the mercury are not spurted out.

Mr. Whopple said that when working with an ordinary "thermometer" tube the contacts were inefficient, owing to oxidation. Moreover, the mercury column broke up, and in some cases mercury clung to the contact-wire. He asked if these difficulties occurred in Mr. Appleyard's apparatus.

Mr. Watson suggested that in some cases the long limb might with advantage be closed. With regard to the dephlegmator he thought that the bends should each be duplicated by a short tube, so as to provide one path for the descending liquid and another for the ascending vapours. This seemed to be the object of the platinum gauze in fractionating-tubes.

Mr. Appleyard, in reply, explained that the change of level in the "tell-tale" was a sudden rise of about an inch of mercury, in a tube about half an inch in diameter. This rise was able completely to envelope the contact-wires, surface oxidation could not affect the working, and there could be no such thing as failure of contact. Moreover, the tube was too wide for mercury to be held up by capillarity. The large area of contact enabled the instrument to be used for strong currents. The cost was small, and the only adjustment consisted in choosing a liquid of suitable boiling-point, for the platinum wires could be sealed in anywhere in the long limb—about 2½ inches from the bottom was a good position for them. The sudden rise occurred when the temperature was one or two degrees above the boiling-point of the contained liquid.

Mr. T. H. Littlewood then read a paper on "*The Volume-changes which accompany Solution*," and described an apparatus for measuring the contraction observed when solids are dissolved in a liquid.

Two glass bulbs are arranged one above the other, so that liquid can pass from the upper one to the lower one through a stopcock, and from the lower one upwards into the neck of the upper one through a second stopcock. This neck, which forms the top of the upper bulb, is fitted with an indiarubber stopper. The lower bulb is tubulured and provided with a glass stopper. A horizontal capillary tube is fitted into the indiarubber stopper, so that volume-changes can be determined, after the manner of using Bunsen's calorimeter. The weighed solid is introduced at the tubulure. The measured amount of water is poured in at the neck. Paraffin oil is now poured in at the tubulure, so that the apparatus is completely filled—the lower bulb with the solid and the oil, the upper bulb with the water. The apparatus is then exhausted, and finally it is placed in a tank of water at constant temperature. When the stopcock between the bulbs is opened, solution begins, and the resulting contraction is measured. For small amounts of salt dissolved in constant volume of liquid, the contraction is very nearly proportional to the amount of salt. For larger amounts, the contraction is greater in proportion than the added salt. If a strong solution is gradually diluted, then, for equal amounts of water added, the contraction becomes smaller for successive amounts of added water. Mr. Littlewood applies Ostwald's theory, and the theory of Van der Waals to the observed results, and expresses the contraction as a logarithmic function of the volumes and the internal pressures.

Mr. Lehfeldt thought the indiarubber stopper was a weak point in the apparatus. With regard to the theory of the contraction, Tammann (*Zeitsch. fur Phys. u. Chem.*, 1895) had given an expression which was rather more intelligible. Tammann found that the effect could be regarded as equivalent to a change of pressure, and, by attributing this quality to the solution, the characteristic surface becomes the same as that for water. The volume of the solution would thus follow similar changes to those that water undergoes with increasing pressures.

Prof. Ewing said the experiments reminded him of the very first piece of research work he had done in physics, which was twenty-five years ago, on the same problem, with Mr. McGregor. An examination of the electrical properties of solutions of certain salts led to an investigation of their changes of density and volume. In some cases the contraction observed was so great that the volume of the solution was less than the original volume of the water to which the salt had been added. They made some measurements, but the apparatus they had used was very rough compared to that described by Mr. Littlewood.

Mr. Watson asked whether Mr. Littlewood had made any simultaneous density measurements. There were some solutions for which the contractions and corresponding densities had been worked out. By examining successive dilutions of strong solutions, and the corresponding densities, a check might be made as to the numerical results obtained by Mr. Littlewood's apparatus.

Dr. Chree suggested that, in place of the logarithmic expression, the total contraction might possibly be better represented by a few terms of a series involving increasing powers of the difference of volume, each term being multiplied by a proper constant.

Mr. Littlewood, in reply, said that the indiarubber stopper possessed advantages in regulating the height of the capillary tube. It did not introduce sensible error, for it was possible to work with it to a centigrm. of mercury in the capillary. On the other hand, temperature-changes of one-tenth of a degree involved 1 centigrm. more or less of mercury in the tube. Bunsen, using an indiarubber stopper, obtained very accurate results in calorimetry.

The Chairman proposed votes of thanks, and the meeting adjourned until February 10th (Annual General Meeting).

CORRESPONDENCE.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

To the Editor of the Chemical News.

In his letter of last week Mr. Brearley asks for my opinion on the fact that a permanganate solution standardised by means of iron gives low results when manganese is being estimated.

Everyone who has tried to standardise bichromate by means of iron wire dissolved in dilute hydrochloric, and more so in sulphuric acid, knows the effect of the traces of carbon present on the "finish." This well-known source of error in the case of bichromate or permanganate I always remove, so that the low results I have obtained cannot be accounted for in that way.

The obvious explanation of course is that the usually accepted equation for the action of permanganate on manganous sulphate does not, in the circumstances under discussion, quite represent the reaction taking place. This is not such an unusual occurrence that it need be classed as anomalous.

In regard to the ignition of Mn_3O_4 in a platinum crucible, Mr. Brearley goes rather astray when he points out that the products of combustion may have a prejudicial effect, as Gooch and Austen (*Am. Journ. Sci.*, 1898, v., 209-214) point out that this is beneficial rather than otherwise.—I am, &c.,

F. W. Daw.

ESTIMATION OF LEAD.

To the Editor of the Chemical News.

Sir,—I have to thank Mr. R. Leffler for his letter *re* "Estimation of Lead."

I had previously tried the molybdate method and found it to work very satisfactory on ores, in which case I evaporated the solution of the ore in a basin with sulphuric acid to near dryness, diluted with water, filtered and treated residue with an acetate, which was then immediately titrated with molybdate, using tannin as indicator.

But in the estimation of such small quantities of lead in slags, with so much iron present, this method is not satisfactory owing to the difficulty of washing the sulphate residue free of iron, which if left in makes the end reaction.

The bichromate method I find excellent if sufficient time is allowed, but which, unfortunately, is not the case.—I am, &c.,

Cox.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 25, December 19, 1898.

This number contains a report of the Annual Public Meeting of December 19th.

The Jecker Prize in Chemistry was divided between MM. G. Bertrand, Buisine, and Daniel Berthelot.

M. Bertrand first worked for some time on the crystalline compounds which give zinc hydrate with the metals

of the alkaline earths. About the same time he identified the colouring matter of pollen with carotene. Since these early researches, he undertook the investigation of lignous tissue, which he found to be essentially different in angiosperms and gymnosperms. During this research he prepared considerable quantities of a sugar, xylose, which was very rare at that time. Xylonobromide of cadmium followed from this; and later, in conjunction with Emile Fischer, M. Bertrand synthesised lixose. His last work was an exhaustive examination of ferments, during which he discovered a new group of these substances, which he called *oxydases*.

Alphonse Buisine began his series of researches by finding, in collaboration with Ed. Duviller, the conditions under which the mono-, di-, and tri-amines of the fatty series are formed, and the methods of separating these amines. His next work was the investigation of the chemical composition of mutton fat. He has also published a method which permits of the preparation of ferric sulphate, ferrous sulphate, and ferric chloride from the residue of pyrites roasting.

Daniel Berthelot in his first published work proposed to apply the method of electrical conductivities to the general investigation of the neutralisation of the principal organic acids, the chief aim being to examine the formation of the neutral salts, acids, and bases produced by the monobasic and polybasic acids, the dissociation under the influence of excess of water, base or acid, and finally, the influence which the different functions exert when joined to the acid function. He has arrived at very interesting results, obtained by the method of conductivities, which agree in the main with those given by thermochemical methods. He has found new methods of investigating the basicity of acids, their functions, and their isomers. Besides these, M. Berthelot has published researches on "The Measurement of Temperature," "Fusion-points of Silver and Gold," "The Determination of Molecular Weights of Gases from their Densities and the Divergence which they show from Marriotte's Law," "Laws of Gaseous Mixtures."

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 11.

Remarks on the Principle of Maximum Work.—D. Tommasi.—The author deduces as the result of his researches, that when a body is submitted to two chemical actions, the reaction which gives off the most heat will always take place by preference if it can be started; and that between two chemical reactions the one which requires the least heat or energy will always take place first, even if it gives off less heat than the other one.

Atomic Refraction of Metals in the Metallic Carbonyls, and the Constitutional Formulæ of these Derivatives.—A. J. Ferreira da Silva.—A controversial paper relating to some remarks by M. Nasini on a previous communication by the author.

Action of Chlorine on Chloride of Ethylene in the yresence of Chloride of Aluminium.—A. Mouneyrat.—250 grms. of perfectly dry chloride of ethylene, $CH_2Cl—CH_2Cl$, was placed with 25 grms. of chloride of aluminium in a perfectly dry flask of 250 c.c. capacity fitted with a vertical condenser. On heating to 80—85°, an abundant disengagement of hydrochloric gas takes place. If this gas is passed through weak potash, to remove the hydrochloric acid, a gas still comes over which is unabsorbed by the potash and can be collected in test-tubes under water; it burns, leaving a deposit of carbon, and if passed into a tube wetted with ammoniacal cuprous chloride a red precipitate is obtained. This gas belongs to the group of acetylenic carbides. It is completely absorbed by bromine, which, when treated with potash, gives a colourless oily liquid, heavier than water, with the formula $C_2H_2Br_4$; that is to say, tetrabromide of acetylene. If the preceding mixture is passed into dry chlorine, this body should combine with the acetylene as soon as it is formed. The colourless liquid obtained is submitted to fractional distillation. Between 84—90° a large quantity of liquid comes over; then the thermometer rises to 130°, and the remainder comes over at 130—150°. The first portion is unattacked chloride of ethylene, and from the other we obtain two liquids, one boiling at 130—136°, and the other at 145—147°. The first contains 84 per cent of chlorine, and is the dissymmetric tetrachloride of carbon, $CH_2Cl—CH_2Cl_3$; the second one also contains 84 per cent of chlorine, and is a symmetrical tetrachloracetylene, $CHCl_2—CHCl_2$.

Chlorisation of Acetylene.—A. Mouneyrat.—In the chlorisation of $CH_2Cl—CH_2Cl$ in the presence of $AlCl_3$, the author has never had an explosion, though in the ordinary way chlorine mixed with acetylene always explodes, and from this fact he thought that by increasing the amount of acetylene in the previous experiment, the return of $CHCl_2—CHCl_2$ might be augmented. Experiment proved this to be the case. Further experiments showed that it was the absence of free oxygen, and of any gas capable of furnishing it, which prevented any explosion.

Preparation of Tetrachloride of Acetylene.—A. Mouneyrat.—In the foregoing experiments the author has shown that explosions are prevented during the preparation of tetrachloride of acetylene by rigidly excluding the air. He now describes a more perfect form of apparatus in which this operation can be carried on, producing as much as 1 kilogrm. in twenty-four hours. It is also pointed out that the chloride of ethylene can be replaced by tetrachloride of carbon, CCl_4, and the $AlCl_3$ suppressed, though the former method is the better one.

Action of Chlorine on Tetrachloride of Acetylene, $CHCl_2—CHCl_2$, in the presence of Chloride of Aluminium. Preparation of Hexachlorsthane (C_2Cl_6).—A. Mouneyrat.—The chloridising power of chloride of aluminium does not depend on the quantity of this body added to the substance to be chloridised, but it is simply a function of the temperature. 250 grms. of tetrachloride of acetylene and 30 grms. of anhydrous chloride of aluminium were placed in a flask as before, and heated in a paraffin bath, and a current of dry chlorine passed through. If kept at 100° for four or five hours only small quantities of hexachlorethane are formed, but if the temperature is raised to 118—120° the action becomes very rapid. The flask soon becomes full of a white substance smelling very strongly of camphor. This is thrown into dilute hydrochloric acid to remove the chloride of aluminium; it is then washed with distilled water, thoroughly dried, and purified by sublimation. It melts in a capillary tube at 187—188°, and contains 89·5 per cent of chlorine. Theoretically, C_2Cl_6 contains 89·8 per cent of chlorine; this body is therefore hexachlorethane.

Constitution of Camphoric Acid and of Camphor.—L. Bouveault.—A very long paper, not suitable for abstraction.

Analysis of Muds Precipitated during the Electrolytic Refinement of Copper.—A. Hollard.—These muds are found to contain gold, silver, salts of arsenic, antimony, lead, bismuth, copper, selenium, and tellurium. They are valuable on account of the large quantities of gold, silver, and copper they contain.

Estimation of Formic Acid in the presence of Acetic Acid and of Easily Oxidisable Organic Bodies.—A. Leys.—Already inserted in full.

Detection of Sawdust in Bread.—G. A. Le Roy.—This falsification is detected by coloured reactions produced on the celluloses by orcine, amidol, indol, pyrrol, &c.

New Suction Pump.—MM. Bourcet and Berlemont.—This cannot be explained without the accompanying diagram.

The Chloridising Action of Ferric Chloride in the Aromatic Series.—V. Thomas.—Already inserted.

MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Arts, 8 (Cantor Lectures). "Bacterial Purification of Sewage," by Dr. Samuel Rideal.
Tuesday, 7th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.
Wednesday, 8th.—Society of Arts, 8. "Nernst's Electric Lamp," by James Swinburne.
Thursday, 9th.—Royal Institution, 3. "Toxins and Antitoxins," by Dr. Allan Macfadyen, M.R.C.S.
—— Society of Arts, 8. "The Penal System at the Andamans," by Colonel Richard Carnac Temple, C.I.E.
Friday, 10th.—Royal Institution, 9. "The Motion of a Perfect Liquid," by Prof. H. S. Hele-Shaw, LL.D.
—— Physical, 5. (Annual General Meeting). Address by the President. "An Ampère-Meter and a Volt-Meter with a Long Scale," by Benjamin Davies.
Saturday, 11th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2046.

ON THE BOILING-POINT OF LIQUID HYDROGEN UNDER REDUCED PRESSURE.*

By JAMES DEWAR, M.A., LL.D., F.R.S.

THE June number of the *Proceedings of the Chemical Society* contains a paper by the author on "The Boiling-point and Density of Liquid Hydrogen." A resistance thermometer made of fine platinum wire, called No. 7 Thermometer, was used in the investigation. It had been carefully calibrated, and gave the following resistances at different temperatures:—

Temperature. °C.	Resistance. Ohms.
+99·1	7·337
+75·3	6·859
+51·4	6·388
+25·7	5·857
+0·7	5·338
−78·2	3·687
−182·6	1·398
−193·9	1·136
−214·0	0·690

The zero of the thermometer in platinum degrees was −263·27°. Mr. J. D. Hamilton Dixon, M.A., Fellow of Peterhouse, who contributed a paper to the *Phil. Mag.* for June, 1898, on "The Reduction of Normal Air Temperature of the Platinum Thermometers," used in the low temperature researches of Professor Fleming and the author, has been good enough to calculate a special formula for this thermometer No. 7. He finds the formula—

$$(R + 43{\cdot}958933)^4 = 2{\cdot}03596488\ (t + 1193{\cdot}1460)$$

expresses the relation between the resistance and temperature in centigrade degrees. This expression gives a probable error of only 0·16° C. over a range of more than 300° C. When this thermometer was placed in boiling hydrogen, the resistance became 0·129 ohm, and remained constant at this value. Calculated into the Dickson formula, this value of the resistance corresponds to a temperature of −238·4° C. If we assume the resistance reduced to zero, then the temperature registered by the thermometer ought to be −244° C. At the boiling-point of hydrogen, therefore, if the law correlating resistance and temperature can be pressed to its limits, a lowering of the boiling-point of hydrogen by 5° or 6° C. would produce a condition of affairs where the platinum would have no resistance, or become a perfect conductor. Now we have every reason to believe that hydrogen, like other liquids, will boil at a lower temperature the lower the pressure under which it is volatilised. The question arises, How much lowering of temperature can we practically anticipate? For this purpose we have the boiling-point and critical data available from which we can calculate an approximate vapour-pressure formula, accepting 35° abs. as the boiling-point, 52° abs. as the critical temperature, and 19·4 At. as the critical pressure; then as a first approximation—

$$\log p = 6{\cdot}8218 - \frac{137{\cdot}9}{T}\ \text{m.m.} \quad . \quad . \quad . \quad 1.$$

If instead of using the critical pressure in the calculation, we assume the molecular latent heat of hydrogen is proportional to the absolute boiling-point, then from a comparison with an expression of the same kind, which gives accurate results for oxygen temperatures below one atmosphere, we can derive another expression for hydrogen vapour-pressures, which ought to be applicable to boiling-points under reduced pressure.

The resulting formula is—

$$\log p = 7{\cdot}2428 - \frac{152{\cdot}7}{T}\ \text{m.m.} \quad . \quad . \quad . \quad 2.$$

Now Formula 1 gives a boiling-point of 25·4° Ats. under a pressure of 25 m.m., whereas the second equation (2) gives for the same pressure 26·1° Ats. As the absolute boiling-point under atmospheric pressure is 35°, both expressions lead to the conclusion that ebullition under 25 m.m. pressure ought to reduce the boiling-point some 10° C. For some time experiments have been in progress with the object of determining the temperature of hydrogen boiling under about 25 m.m. pressure, but the difficulties encountered have been so great, and repeated failures so exasperating, that a record of the results so far reached becomes advisable. The troubles arise from the conduction of heat by the leads; the small latent heat of hydrogen volume for volume as compared with liquid air; the inefficiency of heat isolation and the strain on the thermometer brought about by solid air freezing on it and distorting the coil of wire. In many experiments the result has been that all the liquid hydrogen has evaporated before the pressure was reduced to 25 m.m., or the thermometer was left imperfectly covered. The apparatus employed will be understood from Fig. 1.

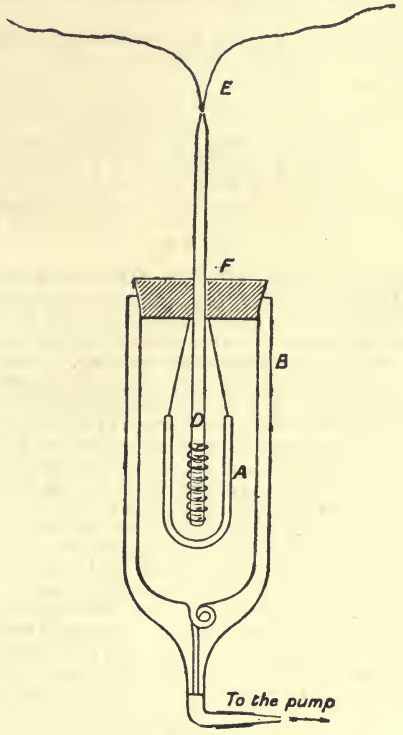

FIG. 1.

The liquid hydrogen collected in the vacuum vessel A was suspended in a larger vessel of the same kind B, which is so constructed that a spiral tube joins the inner and outer test-tubes of which B is made, thereby making an opening into the interior at C. The resistance thermometer D and leads E pass through a rubber cork F, and the exhaustion takes place through C. In this way the cold vapours are

* A Paper read before the Royal Society, December 15, 1898.

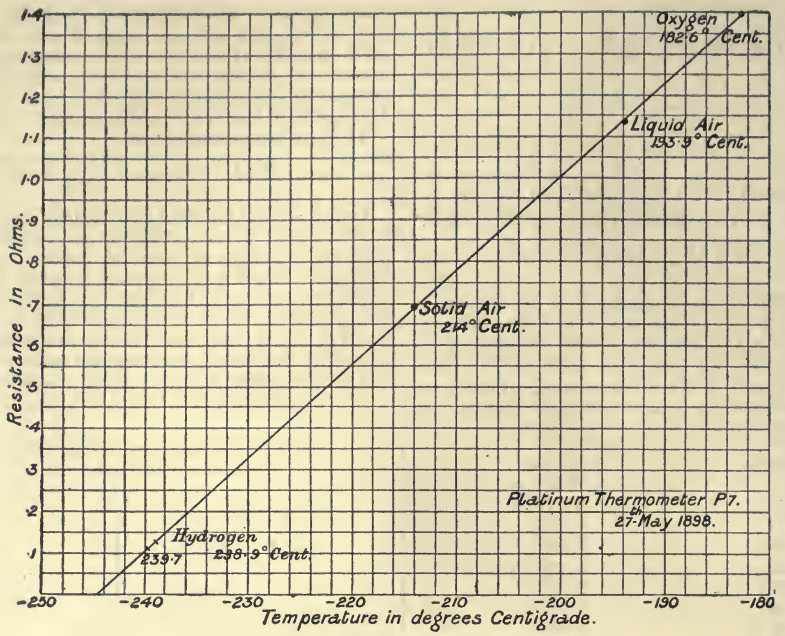

FIG. 2.

drawn over the outside of the hydrogen vacuum vessel, and this helps to isolate the liquid from the connective currents of gas. To effect proper isolation, the whole apparatus ought to have been immersed in liquid air under exhaustion. Arrangements of this kind add to the complication, so in the first instance the liquid was used as described. The liquid hydrogen evaporated quietly and steadily under a pressure of about 25 m.m. of mercury without the least appearance of solidification or loss of mobility; still remaining clear and colourless to the eye. Naturally the liquid does not last long, so the resistance has to be taken quickly. Just before the reduction of pressure began, the resistance of the thermometer was 0·131 ohm. This result compares favourably with the former observation on the boiling-point, which gave a resistance of 0·129 ohm. On reducing the pressure, the resistance diminished to 0·114 ohm, and kept steady for some time. The lowest reading of resistance was 0·112 ohm. This value corresponds to −239·1° C., or only one degree lower than the boiling-point at atmospheric pressure, whereas the temperature ought to have been reduced some 10° C. or in any case 5° under the assumed exhaustion. The position of the observation on the curve of the relation of temperature and resistance for No. 7 thermometer is shown on the diagram (Fig. 2). The question arises then as to what is the explanation of this result? Has the platinum resistance thermometer arrived at a limiting resistance about 35° Ats., so that at a lower temperature it refuses to change in resistance, the curve having become practically asymptotic to the axis of temperature? On the other hand, has the influx of heat by the leads, and the correction on account of this change of resistance become so great as to vitiate the results at these excessively low temperatures? Again, it may be suggested that the thermometer was not properly cooled, or that the liquid hydrogen does not lower in temperature to any marked extent under exhaustion like other liquids. All these conjectures can only be set at rest by a repetition of the experiments with a new thermometer of much higher initial resistance, and under conditions of better heat isolation. No blunder having been detected in the observations, for the present we must assume that the platinum resistance thermometer No. 7 acts in the manner described. It would be premature to discuss the inferences to be drawn from these results until they are confirmed on another variety of platinum wire made into a resistance thermometer. But as this will involve the use of considerable quantities of liquid hydrogen, it will take some time to complete the investigation.

The same kind of anomaly appears in the case of the use of a thermojunction at these low temperatures, but this is a separate matter, and must be dealt with in a further communication.

I am indebted to Mr. J. E. Petavel for assistance in the electrical measurements, and also to Mr. Robert Lennox and Mr. Heath for their general help in the conduct of the experiments.

THE CONSTITUTION OF THE ELECTRIC SPARK.*

By ARTHUR SCHUSTER, F.R.S., and G. HEMSALECH.

WHEN an electric spark passes between metallic electrodes, the spectrum of the metal appears, not only in immediate contact with the electrodes, but stretches often across from pole to pole. It follows that during the short time of the duration of the spark the metal vapours must be able to diffuse through measurable distances.

The following investigation was undertaken primarily to measure this velocity of diffusion with the special view of comparing different metals, and different lines of the same metal.

Feddersen published, in the year 1862, an interesting research, in which photographs of sparks passing between different metal poles are taken after reflection from a rotating mirror. He could from his experiments draw some conclusions which have a bearing on our subject, but it was necessary for our purpose that the light should also be sent through a spectroscope, so as to distinguish

* Abstract of a Paper read before the Royal Society, February 2, 1899.

between the luminous particles of air and those of the metal poles.

The method of the rotating mirror tried during the course of several years in various forms by one of us did not prove successful. On the other hand, good results were obtained at once on trying the method used by Professor Dixon in his researches on explosive waves. This method consists in fixing a photographic film round the rim of a rotating wheel. All that is necessary for its success is to have sparks so powerful that each single one gives a good impression of its spectrum on the film. Were the sparks absolutely instantaneous, the images taken on the rotating wheel would be identical with those developed on a stationary plate, but on trial this is found not to be the case. The metal lines are found to be inclined and curved when the wheel rotates, and their inclination serves to measure the rate of diffusion of the metallic particles. The air lines, on the other hand, remain straight, though slightly widened.

To avoid the tendency of the film to fly off the wheel when fixed round its rim, as in the original form of the apparatus, a spinning disc was constructed for us by the Cambridge Scientific Instrument Company. The film is placed flat against the disc, and is kept in place by a second smaller disc, which can be screwed lightly to the first. The diameters of the two discs are 33 and 22·2 c.m., the photographs being taken in the annular space of 10·8 c.m., left uncovered by the smaller disc. An electric motor drives the disc, and we have obtained velocities of 170 turns per second, though in our experiments the number of revolutions was generally about 120, giving a linear velocity of about 100 metres/second for that part of the film on which the photograph was taken.

The electric discharges were obtained from a battery of six Leyden jars, having a total capacity of 0·033 microfarad, and being charged from an induction machine constructed for us by Mr. H. C. Wimshurst. This machine has twelve plates of 62 c.m. diameter, and give sparks which are 13 inches long.

The electrodes were, as a rule, placed 1 c.m. apart, and an image of the spark was projected on the slit of the spectroscope, the distance of the slit from the electrodes being equal to four times the focal length of the projecting lens, so that the image was equal in size to the spark. The prism used was made by Steinheil, and had a refracting angle of 60°.

We may now pass to the description of the results obtained when the spectrum of a single spark is taken on a moving film. A preliminary trial with various metallic electrodes had shown us that the sharpest results were obtained with zinc, and we therefore chose that metal for our first investigation. The principal lines of zinc as they appear on our photographs are the double line, the least refrangible of the two having a wave-length 4924·8, and the blue triplet, the wave-length of the leading line being 4810·7. All the lines are curved on the photographs taken with the spinning disc, but the displacements, especially near the poles, are subject to considerable variations. This is probably due to the fact that the path of the metallic particles is not always straight, and, if straight, its image does not necessarily coincide with the slit. A very slight error in measurement will also affect the results considerably when the total displacement measured is small. Our results do not for this reason allow us at present to give any opinion as to the maximum velocity of the particles near the pole; but if these are considerable, they drop down very quickly to speeds which, in the case of zinc, are not far off 500 metres/second.

We have adopted two methods of comparison between different photographs. We have in the first place measured the displacements at a number of nearly equidistant points, and from these measurements we have deduced the time taken for a metallic molecule to pass from the pole to a point 2 m.m. away from it. If this method could be applied in every case it would form a rational and consistent basis of comparison. But the curved lines which are to be measured are often very diffuse near the pole; this, and the continuous spectrum, may render it impossible to obtain satisfactory measurements at that point. In order not to have to reject unnecessarily a large number of measurements because the spectrum near the pole was indistinct, we have adopted another method, which, though less rational than the first, is found to give consistent results. From all our measurements we may deduce certain figures for the molecular velocities at different and generally equidistant points on the photographs, and may take the average of all these figures as the mean velocity of the particle. In the following tables, V_1 will always refer to the mean velocity between the pole and a point 2 m.m. away from it, while V_2 refers to the average velocity taken for different distances, as just explained. The influence of change of capacity and change in the length of the spark was investigated in the case of zinc, and the following tables exhibit the results. As the zinc lines are sharp near the pole, the first of the above methods of measurement could be applied.

Table I.—*Average Velocity* (V_1) *in metres/second of Zinc Molecules.*

Sparking distance. C.m.	Wave-length.	Number of jars. 2.	4.	6.
0·51	4925	814	556	416
	4811	1014	668	529
1·03	4925	400	499	415
	4811	501	548	545
1·54	4925	723	1061	435?
	4811	1210	1526	492?

The first striking result to be deduced from the table is the uniformly higher velocity deduced from the double line 4925, as compared with that found when one of the lines of the triplet is measured; for we have ascertained that the two first lines of the triplet are always displaced by the same amount, and the third is so much mixed up with the air lines in its neighbourhood that it cannot be measured. It was one of the objects of the investigation to detect, if possible, differences of this kind, which might be accounted for by the fact that the molecules producing different lines of the same spectrum have not necessarily the same mass. We nevertheless hesitate to ascribe the smaller apparent velocity derived from $\lambda=4925$ to this reason. This line, as has been mentioned, is one component of a double line, and the doublet is not resolved on the photographs taken with the moving film. Near the pole where the light is strong, the edge of the least refrangible component of the doublet would be considered to be the least refrangible edge of the doublet; but near the centre of the spark the light is weaker, and the lines, owing to the motion of the wheel, are drawn out towards the violet. The most intense portion of the image will here be that part where the two lines are superposed, and in wishing to set the cross wire on the edge of the line, we should be tempted to set it on the edge of the *most* refrangible component. There is reason to believe that this is the cause of the greater deflection of the double line, and the photographs show some signs that if this source of error is eliminated, the molecule giving out the double line moves more quickly than that giving rise to the triplet. We reserve the decision of this point until we have been able to apply greater dispersion.

Comparing the sparks obtained with different capacities, it is found that when the spark gap is small there seems a very curious *diminution* of velocity as the capacity increases; this is not what should have been expected at first sight, as with the large number of jars we should expect higher temperatures, and therefore greater velocity of diffusion. When the spark gap is 1 c.m., the experiments do not reveal any marked change due to capacity. When the gap is increased still further the sparks become very irregular and unsteady, and no certain conclusions can be drawn from our measurements; the numbers

marked with a query are specially doubtful. When six jars are used practically identical numbers are obtained for all sparking distances, but with small capacity the centimetre spark seems to give a lower result than in the two other cases. While we should not like at present to consider this as an established result, the table serves to show that the centimetre spark and the highest capacity used gives the most consistent numbers, and our experiments with other metals were all made under these conditions, except in the case of bismuth, where clearer spectra were obtained with only two jars.

Comparing different metals with each other, we find in the first place that those having comparatively low atomic weights, viz., aluminium and magnesium, have higher molecular velocities. With magnesium the metal vapour is scattered about to such an extent that no measurements could be made, but the average velocity of the aluminium molecule was found to be over three times as great as that of zinc, the numbers not laying any claim to accuracy. Comparing zinc and cadmium with each other we obtain almost identical numbers, both for the corresponding doublet and triplets.

Bismuth gave remarkable results. In spite of its high atomic weight some of the lines are but little displaced, indicating an average molecular velocity of 1420 metres/second. For other lines the velocity falls down to that of zinc and cadmium, while one line ($\lambda=3793$) has a still lower velocity.

We have not obtained satisfactory results with mercury; the best were those in which poles used were of zinc or cadmium, which were covered with amalgam. Differences in molecular velocities were obtained for different lines, but the result here is not so certain as with bismuth.

There is obviously no simple law connecting these velocities with the atomic weight.

Dr. Feddersen was led through his researches to the conclusion that the metallic particles after being once torn off from the electrodes by the discharge took no further part in it, were thrown irregularly into the space surrounding the electrodes quite independently of the electric current. Although in some cases, and especially with magnesium poles, there is some evidence that this is partly true, we are led to take the following modified view of the matter.

The initial discharge of the jar takes place through the air; it must do so because there is at first no metallic vapour present. The intense heat generated by the electric current volatilises the metal which then begins to diffuse away from the poles; the subsequent oscillations of the discharge take place through the metallic vapours and not through the air. We find confirmation of this view in a striking experiment which is easily repeated. If a coil of wire be inserted in the spark circuit of a Leyden jar, which may be charged either by a Wimshurst machine or an induction coil, the air lines disappear almost completely, the metallic lines alone remaining; the nitrogen line at 3995 is the only one which seems to remain with undiminished vigour. According to our view we should explain the experiment by saying that the coil which adds self-induction lengthens the duration of the discharge, and allows time for the metallic molecules to diffuse properly into the spark gap. A great part of the energy of the current may then do useful work by heating up the metallic molecules instead of those of air. Mr. Hemsalech is at present engaged in investigating the changes in the metallic spectra which accompany the insertion of self-induction.

The first spark passing through the air will give rise to a sound wave which, during the complete time of the discharge, will only travel a few millimetres. We may therefore consider that the mass of metallic vapours suddenly set free is driven by its own pressure into the partial vacuum formed by the heated air. It would seem more correct to liken the process to that of a gas under pressure flowing into a vacuum than to that of a pure thermal diffusion. There is not much difference between these views, and we may take it that in our experiment we have approximately measured the velocity of sound in the metallic vapours. This gives a relation between their temperature and density. If we neglect the differences in the rates of specific heat we find approximately—

$$V = 80\sqrt{T/\rho},$$

where T is the absolute temperature, and ρ the vapour density referred to hydrogen. Thus for cadmium the average molecular velocity found was 560, and substituting $\rho=56$ we obtain $T=2700$, which seems a possible value. Hence we conclude that the molecule of cadmium in the spark cannot have a mass which is much smaller than that directly determined near the boiling-point of the metal.

In conclusion we have also taken some photographs in which the slit was directly focussed on the sensitive film without the interposition of the film. The photographs show a straight image of the slit followed by a number of curved bands extending from both poles into the spark gap.

The straight image we consider to be the initial discharge through air creating sufficient heat to fill the space with vapour through which the oscillating discharges may then pass. Our experiments point to the fact that the periodic time was rather too small in our experiments to give the best results. The metallic molecule before it has had time to reach through a sufficient distance was possibly affected in its motion by the subsequent oscillation. We hope to remedy this defect by introducing still higher capacities than those used. Our experiments allow us to give the following approximate numerical data. The air rendered luminous by the first discharge remains luminous for a time of about 5×10^{-7} seconds, the metallic vapours then begin to diffuse and reach the centre of the spark (the gap being 1 c.m. long) in a time which, in the case of cadmium, was about 6×10^{-6} seconds. The periodic time of the oscillations with our six jars and a circuit possessing as little self-induction as possible was about 2×10^{-6} seconds. The metallic vapours remain luminous in the centre of the spark for a longer period than near the poles, the duration of the time during which some luminosity can be traced with a discharge from six Leyden jars is about $1{\cdot}5\times10^{-5}$ seconds.

NOTES ON THE ESTIMATION OF TUNGSTEN.

By HARRY BREARLEY.

In his paper (Chemical News, vol. xxiv., p. 175) on the "Estimation of Molybdic Acid as Plumbic Molybdate," Chatard remarks that "analogy would seem to offer a good method for tungstic acid, and experimental analyses were made for this purpose, but after repeated trials the process was finally abandoned, as the precipitate came down so finely divided that it passed through the filter. The precipitation, however, seems to be complete, and I have hopes that with closer filter paper greater success will be obtained."

Chatard's difficulty of thirty years ago has long since been overcome, both in the matter of filter-papers* which

* The precipitate easily subsides without the addition of alkaline salts, so that until it is actually on the filter there is no difficulty. With pulp filters, which I use wherever possible, the washing is a very tedious operation unless suction is used. In the latter case, and with pulp filters, the suction may be strongly and safely applied, the washing is so agreeably rapid that added alkaline salts are quite dispensable. The suction referred to is not generally applied as usual by means of the filter-pump, but by arranging a flask as usual for pressure filtering and sucking with the mouth by means of a piece of rubber tubing attached to the bent glass tube which passes through the stopper. In this way, with a flask of several hundred c.c. capacity, it is possible to obtain a partial vacuum equal to 12 inches of mercury; and as, using pulp filters, the vacuum is destroyed only by the wash-water passing through the precipitate, one rarefaction can be made to serve for one complete washing. Ordinary rubber tubing closes up under a pressure of 9 to 12 inches of mercury.

would have filtered his identical sample, and by the addition of ammonium salts, which have been shown to make the precipitate more easily filterable.

The inducement to re-examine the precipitation of tungsten as lead tungstate lay in the fact that the amount of ($PbWO_4$ and $PbMoO_4$) precipitated from a known mixture of tungstic and molybdic acids under such circumstances as had always precipitated molybdic acid alone as true $PbMoO_4$, led to the conclusion that the lead tungstate was not strictly represented by the formula $PbWO_4$, and further that the general analogy which Chatard foresaw did not go very far. When it is remembered that tungsten and molybdenum in a mixture are frequently estimated by precipitating them together as lead salts, directly estimating the one and arriving at the other by difference, then the importance of settling the point becomes apparent.

The method of analysing the lead tungstate may be as well described at the outset. The principle involved will be made—has already been made in fact—the basis of a separation of tungsten and molybdenum.

On boiling ignited lead tungstate with a large excess of concentrated hydrochloric acid it is dissolved to a clear solution. On continued boiling an opalescence forms, deepens, and would become yellow through precipitated tungstic trioxide. Before this point is reached, providing only that the solution be opalescent, dilution with four or five times the acid's volume of water, and subsequent boiling for a few minutes, throws down *all* the tungsten as trioxide. This precipitate is soluble in concentrated hydrochloric acid, it is very easily filtered, and unless the turbidity, previous to the addition of water, has become yellow it does not stick to the sides of the beaker. The addition of nitric acid throws down WO_3 even from the concentrated hydrochloric solution, but generally its presence causes an irremovable deposit on the sides of the beaker. It might also be found that simply boiling with dilute hydrochloric acid would decompose the lead tungstate, and leave only the WO_3 behind.

After washing the WO_3 with very dilute hot hydrochloric acid (pure water causes it to pass through the filter) pulp and precipitate are ignited together; the residue has a beautiful pale yellow colour. In the filtrate the lead may be determined by neutralising with ammonia, making acid with acetic, and precipitating with a perfectly clear solution of sodium or ammonium molybdate in the manner previously described (CHEMICAL NEWS, lxx. x., 14).

The difficulty of working through a series of operations in *perfectly* neutral solutions is well known. The presumed analogy was therefore tested in the first place by observing the precipitation of lead tungstate in a solution acidified with acetic.

Since approximately pure alkaline tungstates are difficult to obtain, and as according to Smith and Oberholtzer (CHEMICAL NEWS, lxviii., 6) and other authorities the purest tungsten compounds obtainable, even the "wolframsaure puriss" contain molybdenum, the standard solution was prepared from a carefully analysed metallic tungsten powder. Previous to fusion with soda carbonate it was ignited for a long time, so as to volatilise any Mo or MoO_3 which it may have contained. I have to thank Mr. R. L. Leffler for repeatedly confirming the strength of my standard solutions by an independent method.

The amount taken for each test should theoretically yield 0·2588 grm. of $PbWO_4$. The ratio $PbWO_4 : WO_3$, by which, after analysis, the nature of the compound is determined, is 1·962 if Pb = 207, W = 184, and O = 16.

The Influence of Acetic Acid.

With an excess of only 1 c.c. of acetic acid in a solution measuring about 300 c.c., the $PbWO_4$(?) after ignition weighed only 0·2384 grm., and yet on analysis yielded an amount of WO_3 (0·1320 grm.), corresponding exactly to the theoretical amount (0·2588 grm.) of lead tungstate. Here the ratio $PbWO_4 : WO_3$ is only 1·806. A like result repeated itself with each successive experiment carried out in a similar way. Finally by precipitating with a known amount of lead and estimating the excess a similar result was arrived at. The excess and that combined with the WO_3 making up the amount added, but both alike pointing to the acid character of the precipitated lead tungstate. Thus test upon test showed that in what might be called a faintly acetic solution of alkaline tungstate, the precipitate formed by lead acetate is never $PbWO_4$, but an acid compound $PbWO_4.xWO_3$.

Experiments carried out in more strongly acidified solutions gave the following results:—

Excess acetic.	Grs. $PbWO_4$ (?).	Grms. error.	WO_3 obtained on analysis.	$\frac{PbWO_4\ (?)}{WO_3}$.
1	0·2384	0·0204	0·1320	1·806
10	0·2190	0·0398	0·1305	1·678
30	0·1900	0·0688	0·1210	1·570

By very long-continued boiling a further precipitate could be formed in the very acid filtrate from the lead tungstate, but it was only small compared with the deficiency, and any hope of completing the precipitation is never likely to be realised in that way.

The acid character of precipitated lead tungstate is not peculiar to acetic solutions. It seems generally to be the case if the precipitation is performed in an acidified medium. Thus if a solution of alkaline tungstate be faintly acidified with nitric acid, as is customary when precipitating tungsten with mercurous salts* (Blair, "Chem. Anal. of Iron," p. 193) and precipitated with a solution of lead nitrate, using mercuric oxide to destroy the last traces of acid, the resulting lead tungstates are decidedly acid. Of the following, Example I. contained a large amount of ammonium nitrate, II. contained none.

	Grs. $PbWO_4$ (?).	Error.	WO_3 on analysis.	$\frac{PbWO_4\ (?)}{WO_3}$.
I.	0·2460	0·0128	0·1310	1·878
II.	0·2270	0·0318	0·1320	1·720

One of the precipitates contains precisely, and the other nearly, the whole of the added tungsten, in spite of the enormous deficiency of the weighing as $PbWO_4$.

Now that the acid character of lead tungstate formed under these circumstances has been established, the fact does not seem so surprising, except in its intensity, nor is an explanation far to seek. The peculiarity would seem to depend entirely on the fact that lead tungstate is easily decomposed by very dilute acids, and that its formation in an acidified solution offers the most suitable occasion for illustrating this. In order to further elucidate the point a series of experiments were performed under the same conditions as those of Table I., except that instead of adding the lead acetate to a hot acid solution of the alkaline tungstate it was added to a slightly alkaline solution, the excess of acetic acid being added later; in this way was formed a true, or probably a somewhat basic lead tungstate. The results tabulated show that, besides decomposing lead tungtate, the larger amounts of acetic acid either dissolve some of the liberated WO_3 or else dissolve some of the lead tungstate undecomposed.

Excess acetic.	Grs. $PbWO_4$ (?).	WO_3 on analysis.	$\frac{PbWO_4}{WO_3}$:
1	0·2430	0·1320	1·841
10	0·2320	0·1314	1·766
30	0·2160	0·1280	1·687

Precipitation of Lead Tungstate from Neutral Solutions.

Neutral alkaline tungstates precipitated with neutral lead acetate invariably gave precipitates which were

* The results being given raise the question as to whether or not the precipitate is accurately described as "mercurous tungstate." The question has no bearing on the results obtained, as all the mercury is volatilised on ignition, and the tungsten calculated from the remainiug WO_3.

somewhat basic. The error was generally about 2 per cent. The ignited precipitates always yielded on analysis as much WO_3 as corresponded to the amount of material taken.

The excess of PbO may be due either to the decomposition of the excess of lead acetate into acetic acid and lead protoxide, a change acetates in hot neutral solutions are very prone to (see Watts's "Dictionary," vol. i., p. 9, and Chem. News, lxxvi., 223), particularly when a precipitate is being formed in their solution; or, as has been pointed out (Watts's "Dictionary," i., 11), the aqueous solution of lead acetate is partially decomposed by the CO_2 of the air, lead carbonate being precipitated, and a portion of acetic acid set free. Alkaline tungstates, too, are never perfectly free from CO_2, and, further, the neutralisations in presence of large amounts of alkaline salts, using methyl orange as indicator, is, according to Thomson (Chem. News, xlvii., 126), not quite coincident with actual neutrality; so that absolutely neutral solutions are only obtainable with difficulty, and even then the correct precipitate is not assured.

Working still in neutral, or as near as practicable neutral, solutions, the influence of various alkaline salts, since they always accumulate in an analysis, was observed.

Am. chloride. Grs. added.	$PbWO_4$.	Error.	WO_3 on analysis.	$\frac{PbWO_4}{WO_3}$.
2	0·2155	0·0433	0·1120	1·920
5	0·1580	0·1008	0·0805	1·963
Am. nitrate.				
2	0·2580	0·0008	0·1314	1·963
5	0·2540	0·0048	0·1315	1·931

Acetate exerts a decidedly solvent action, but not nearly so marked as the chloride. The results show that ammonium chloride should always be avoided. The results with ammonium nitrate are in general agreement with those of Smith and Bradbury (*Berichte*, xxiv., 2093), who found $PbWO_4$ to be insoluble in solutions of that salt. The acidity of the lead tungstate in the first and last results are certainly not due to any peculiar influence exerted by those particular amounts of salts, but probably to an imperfect neutralisation. It is scarcely credible what small amounts of acid affect the basicity of the precipitates.

As many compounds of tungsten must be attacked by fusion, the influence of salts of the fixed alkalis are appended.

Soda chloride. Grs. added.		$PbWO_4$.	Error.	WO_3 on analysis.	$\frac{PbWO_4}{WO_3}$.
2	(*a*)	0·2550	−0·0038	0·1295	1·969
	(*b*)	0·2620	+0·0032	0·1310	2·000
5	(*a*)	0·2020	−0·0568	0·1010	1·974
	(*b*)	0·2110	−0·0478	0·1050	2·009
Soda nitrate.					
2		0·2570	−0·0018	0·1310	1·962
5		0·2540	−0·0048	0·1310	1·939
Potass. nitrate.					
5		0·2594	0·0006	0·1312	1·979

Soda chloride exerts a remarkable influence. Up to about 2 grs. (vol. of solution 300 c.c.) the error introduced is not very great, and under some circumstances would be allowable. In the sample containing 5 grms., however, the filtrate on re-boiling becomes cloudy with a further precipitate, and successive precipitates may be formed and filtered off time after time, but never when aggregated do they approximate theoretical demands so nearly as would make the presence of soda chloride with long boiling tolerable. In the table samples (*a*) were just raised to boiling, (*b*) were boiled several minutes. The precipitates of the latter are decidedly basic.

How shall the precipitation of tungsten as a lead salt be made available for accurate analytical purposes? It is of little moment whether the precipitate have an acid or a basic character so long as it contains the whole of the tungsten, if one cares to go a step further and separate the WO_3 by treatment with hydrochloric acid, &c. To this end the precipitation may be made from a solution acidified slightly with acetic acid, or with nitric acid using mercuric oxide to take up the excess, or even from a solution made faintly alkaline with or without the further addition of acetic. In any case the tungstic acid will be an accurate measure of the tungsten originally present.

To throw down the tungsten under such conditions as would assuredly lead to an ignited precipitate which was really $PbWO_4$ was the object in view when the influence of ammonium chloride was observed. As that salt is not available, ammonium nitrate must be made to serve the same purpose. On adding lead acetate to an ammoniacal solution of dilute ammonium chloride or nitrate, the basic precipitate which forms in the cold is completely dissolved as the excess of ammonia is driven off by boiling. If, then, to the alkaline tungstate there be added 2 or 3 grms. of ammonium nitrate, a faint excess of nitric acid (boil a few minutes), a small excess of ammonia, and an excess of lead acetate, we shall have formed $PbWO_4$ mixed with a little basic lead compound. This latter body is redissolved by a few minutes' brisk boiling, and the true $PbWO_4$, which becomes denser by the boiling, may be filtered off, ignited, and its weight used for the calculation of the tungsten.

The following are a few such tests calculated, I. from the weight of $PbWO_4$, and II. from the WO_3 obtained after decomposing that precipitate with hydrochloric acid.

Tungsten added. Grs.	Tungsten found. I.	II.
0·2093	0·2081	0·2086
0·1046	0·1043	0·1044
0·0523	0·0526	0·0522
0·0209	0·0212	—

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PREPARATION OF ARSENIC HYDRIDE.

By A. P. SAUNDERS.

Having occasion some time ago to prepare considerable quantities of the hydride AsH_3, the writer devised a method based on that of Janowsky (*Ber.*, vi., 219), but differing from this in certain particulars, which make it perhaps worth noting.

The method of Janowsky consists in first preparing arsenide of sodium by passing the impure hydride obtained from zinc arsenide and sulphuric acid over heated sodium, and then decomposing this compound by means of water or dilute acid. This method of preparing the arsenide of sodium is, however, difficult and tedious. A much simpler way is by heating together the two elements in question. This is effected in the following manner:—A porcelain boat is filled with arsenic in powder or very small fragments, and upon it are placed a few small pieces of freshly-cut sodium; the boat is then immediately placed in a piece of wide combustion-tubing, protected inside by a strip of asbestos upon which the boat is placed. The ends are loosely plugged, and the tube then slowly heated with a burner. When the heating has been carried up to such a point that the glass just begins to redden, the reaction takes place suddenly and with great violence, so that the glass tube is not unfrequently cracked; for such emergencies it is well to have a large vessel of copper sulphate solution at hand in the hood, since arsenide of sodium is at once decomposed by moisture forming the hydride. If the operation is successful, the tube may be closed and laid aside to cool. The reaction is somewhat cleaner if carried on in a stream of hydrogen, but, as a little sodium oxide or hydroxide does not finally affect the result, this precaution is unnecessary.

A convenient form of apparatus for generating the gas may be made by sealing on to a wide tube, ending above in a stopcock, a side tube set on at an angle, and sufficiently large to allow the porcelain boat with its contents to fall freely through it into the bottom of the main tube. Such an apparatus is first filled with dilute hydrochloric or sulphuric acid, and the boat is then allowed to drop in by the side tube: the gas generated collects in the top of the main tube, and may thence be transferred to other vessels.

In filling the boat care must of course be taken that arsenic shall be present in considerable excess, so that no free sodium may remain.

In using this method no effort was made to get the gas quite free from hydrogen; nevertheless it appeared, by absorption with copper-sulphate solution, to be over 90 per cent pure; hence the method could probably be modified to produce the hydride in almost or quite pure condition.

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GÜNZBURG'S REAGENT APPLIED TO THE DETECTION OF HALOGENS IN ORGANIC COMPOUNDS.

By P. N. RAIKOW.

About ten years ago Günzburg proposed the use of an alcoholic solution of phloroglucine and vanilline for the detection of free hydrochloric acid in the gastric juices.

This reagent remains unchanged by heat, under the influence of the organic acids, while even a trace of free hydrochloric acid is sufficient to cause an intense red colouration.

The mixture of phloroglucine and vanilline can also be used for the purpose of detecting the presence of halogen bodies in organic substances; but it must be mentioned that these combinations, heated directly with the reagent, rarely give the characteristic red colouration. But in submitting the products of the combustion of the organic halogen compound to careful examination, we can detect with certainty the least trace of the haloid acids formed.

When the organic matter is liquid and inflammable, a small quanitity is placed at the bottom of a flat porcelain dish, a few drops of the reagent are added, and the alcohol set alight. In the case where the substance is a halogen compound the contents of the crucible take an intense red colour, but when halogens are absent no colouration is noticeable.

Thus, for example, we can recognise with certainty the presence of halogens in the following substances:—$CHCl_3$, CCl_4, C_2Cl_4, C_6H_5Cl, and $C_6H_4Br.CH_3$; but in some compounds, such as C_6Cl_6 and $3C_6Cl_4O_2$, we cannot detect chlorine by this method.

We can, however, detect the presence of haloid bodies in all halogen compounds by proceeding in the following manner:—Rinse a small porcelain crucible with the reagent, throw away the excess, and set light to the small quantity of alcohol remaining in the crucible, or it can be left to spontaneous evaporation.

The phloroglucine and the vanilline which were in solution remain in the crucible in the form of a thin colourless layer. Turn the crucible upside down over a spirit lamp, so that the flame licks, so to speak, the layer of phloroglucine-vanilline, and, by the aid of a copper or platinum wire, hold a small quantity of the substance under examination in the flame. If a haloid body is present, the characteristic colouration will be produced in the crucible.

When the subject of examination is a gaseous body, two cases may occur. Either the gas is inflammable, when it can be lighted at once; or it is not inflammable, and it must be brought into the flame of the spirit lamp over which the crucible containing the layer of phloroglucine-vanilline is held.—*Chemiker Zeitung*, 1898, No. 4, p, 20.

DETERMINATION OF THE SOLIDIFICATION-POINT OF PARAFFINS.

By R. KISLING.

In commercial transactions it is the solidification-point that is chiefly considered in estimating the value of paraffins; the other factors—such as colour, odour, transparency, &c.—play only a secondary part.

Numerous methods have been proposed for determining the point of solidification of paraffins, but such care must be taken, and so many precautions are necessary, that they lose much of their value and simplicity.

For this reason I have devised a new method, at once simple and exact, and which does not take longer than ten minutes to perform. The only fault that can be found with my process is that it requires at least 50 grms. of paraffin to carry it out.

The apparatus I employ consists of a glass cylinder we will call A, 12 c.m. high and 8 c.m. in diameter; a flat piece of wood or cardboard is placed on this cylinder, and has a central hole, destined to hold a precipitation glass, which we will call B; its height is about 8 c.m. and its diameter about 5 c.m.

In B we place 50 grms. of clear paraffin, filtered if necessary; heat on the water-bath to a temperature of about 10° higher than the solidification-point of the paraffin, and place it in the larger cylinder in such a manner that it is suspended by its rim in the hole through the cardboard. The melted mass is stirred by means of a thermometer until a small pellet of solid paraffin is formed in the centre of the bottom of the glass. We may be sure that the solidification-point has now been reached, because immediately afterwards the whole of the bottom of the glass becomes covered with a thin layer of solid paraffin in such a manner that streaks may be made with the thermometer. At the same time flakes of paraffin appear throughout the mass. The test may be repeated several times with the same sample.

To catch the critical point exactly, it is better to look through the side of the glass rather than down from the top.

The results obtained are perfectly concordant, and do not vary by one-tenth.

I may point out that the method is equally applicable to the determination of the point of solidification of ceresine, stearine, and solid fats, &c.—*Chemiker Zeitung*, 1898, p. 209.

THE COLORIMETRIC ESTIMATION OF COPPER.

By M. LUCAS.

A solution of a copper salt gives a reddish-brown colouration with ferrocyanide of potassium. If the solution is weak the precipitate will only collect very slowly, and leaves the solution clear, but of a red colour. It is this colouration, ten times more sensitive than that given by ammonia, that can be utilised for the estimation of small quantities of copper.

M. Jagnaux has shown (*Anal. Chim.*, p. 451) that it is necessary to treat acid solutions of copper with ammonia, and to boil them until they have a neutral reaction. Then place a few drops of ferrocyanide of potassium in two test-tubes, pour into one a known volume of the solution to be examined, and bring the liquid in both test-tubes to the same level by adding distilled water; add 0·5 grm. of nitrate of ammonium, then, to the tube containing distilled water, add a titrated solution of copper until the

tints in the two test-tubes are identical. The tests are made under the following conditions:—

1. The solution under examination contains more nitrate of ammonium than the tube for comparison.
2. The ferrocyanide of copper is in one case formed in a small volume of liquid; the solution, then diluted, gives a different colouration to that which is obtained in the definite volume.
3. Nitrate of ammonium added after the reaction does not change the colour, though if added beforehand it gives a milky rose-coloured appearance, a more intense colouration, and a precipitate which collects very rapidly.
4. If the solution to be examined contains hydrochlorate of ammonium, boiling causes a loss of copper; if it contains nitrate of ammonium, the copper may be precipitated in the state of basic nitrate, and will no longer give a uniform colouration.

Sufficiently accurate results can be obtained by always working under the same conditions; a scale of comparative colours can be made by adding the same volume of nitrate of ammonium as there is in the solution being tested, and diluting to the same volume; the ferrocyanide of potassium is added to all the tubes simultaneously, and the colourations are compared immediately. It is, however, better to prevent the presence of other salts by evaporating the hydrochloric solutions to dryness, taking up with water, and titrating from a burette filled with the typical solution containing 1/10,000th of bichloride of copper. In this manner I obtained the following results:—

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Amount taken	5·0	7·0	5·0	4·0	3·5	9·0	5·0	3·5	8·5	8·3
Amount found	4·8	6·5	5·0	4·0	3·8	8·5	5·0	3·0	8·0	8·0

I have applied this method to the estimation of oxygen in commercial copper.

a. Estimation of Oxygen in Copper.—The metal is treated with nitrate of silver, and the precipitate, separated from the filter in the way I have described in a previous communication, is treated with a boiling solution of hydrochloric acid at 5 per cent.; this dissolves the basic nitrate of copper: filter, evaporate to dryness with a few drops of sulphuric acid, take up with nitric acid, separate the copper by electrolysis, dissolve it in nitric acid, evaporate to dryness with hydrochloric acid, take up with 100 c.c. of water, and add 5 drops of a 5 per cent solution of ferrocyanide of potassium.

To 100 c.c. of water and 5 drops of ferrocyanide of potassium add, with a graduated burette, a solution of bichloride of copper (Cu = 0·1 grm. per litre) until the colour in each tube is identical, taking care to keep the two liquids at the same volume.

The number of c.c. of bichloride of copper run in represents the number of tenths of a m.grm. of copper.

Electrolysis seemed to me to be necessary for separating the copper from the iron; it is the only possible method when using sulphydric acid at 70°. Separation by ammonia, even when repeated several times, is incomplete, but this inconvenience would be negligible. It, however, introduces salts of ammonia, which, it is true, can be reproduced in the comparative tubes, but this is nevertheless very unfavourable to the reaction; they cannot be driven off by volatilisation without causing a loss of copper.

b. Estimation of Copper in Wrought Iron, Steel, and Iron Castings.—The copper, electrolysed directly in nitric solution, is re-dissolved, and electrolysed a second time to separate all traces of ferric oxide.

This deposit is estimated colorimetrically by the same method as in *a*; the electrolysis of 1 grm. of metal may give a deposit of less than 1 m.grm. of copper.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 18-19.

ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 53).

It is obvious that, if the oxide is really dissociated, it should be capable of conducting electricity, because of the presence of traces of metal. In order to test this point, small platinum electrodes of 0·25 square c.m. in area and separated from one another by about 0·5 c.m., were packed in pure specimens of the several oxides. Each porcelain crucible containing an oxide was gradually heated, after having placed the two electrodes in a circuit with a delicate amperemeter and four accumulators. When cold, the resistance of each of the oxides was at least 200,000 ohms. Upon heating, the cupric oxide began sensibly to conduct below a red heat, and at about 650° offered only about as much hindrance to the current as was afforded by 550 ohms, remaining constant at that point. On the other hand, zincic oxide fell in resistance only to about 15,000 ohms at 650°, and required fully 900° to bring it as low as 1000 ohms; while the highest heat of the blast-lamp could not cause the magnesic oxide to transmit as much as the twentieth of a milliampere, the least current capable of being observed upon the amperemeter. It is needless to say that any possibility of the presence of a reducing atmosphere was excluded, and the fact that each oxide returned almost if not quite to its non-conducting state after cooling is sufficient proof that the heat alone was the cause of the phenomena observed. These interesting results are fully in accord with the hypothesis that cupric oxide is slightly dissociated at a red heat, that zincic oxide is less dissociated, and that magnesic oxide, retaining its occluded oxygen with great obstinacy, is scarcely dissociated at all. Magnesic oxide, being one of the stablest of all compounds at high temperatures, could not be expected to show any appreciable dissociation or conductivity; and the wonder is, that the occluded gas is able to escape even as fast as it does.

This assumed partial thermal dissociation of solids must not be confounded with electrolytic dissociation (ionisation); for the energy which determines the separation of the components in the present case is heat, and not electricity. The conductivity is not electrolytic conductivity, but only the metallic conductivity of the metal set free by a purely thermal dissociation. In order to prove this, a current of 20 milliamperes was transmitted through cupric oxide for three hours. This quantity of electricity would have carried nearly 70 m.grms. of copper from a cupric solution, and since neither copper nor an oxide appeared adhering to the platinum negative electrode, it is safe to infer that the conductivity is not electrolytic. While these oxides thus conduct electricity without transference of material, it is undoubtedly true that many substances—even glass for example—which are non-conductive when cold, become capable of carrying a current *electrolytically* when heated. Melted salts are well known to be good electrolytic conductors, and Graetz (*Wied. Ann.*, 1890, vol. xl., 18), has found that this conductivity begins before the salts have melted. Our knowledge of the *rationale* of these facts is altogether too incomplete to afford satisfactory explanation of all the phenomena attending the passage of electricity through solids, liquids, or gases at high temperatures; and it is perhaps unsafe to record the conductivity of cupric oxide as a definite indication of the temporary presence of metallic copper in the case under discussion.

Following is a more certain proof that this dissociation is to be considered as analogous to the decomposition of

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxiii., No. 22; also *American Chemical Journal*, November, 1898.

limestone by heat. Here, as there, the gas, in the present case oxygen, must have a definite pressure of dissociation; but no appreciable amount of metal or lower oxide can form when the tension of the oxygen in the surrounding atmosphere is greater than this definite pressure. On the other hand, cupric oxide should lose not only its occluded oxygen, but all the oxygen that normally belongs to it, leaving metallic copper (or at least cuprous oxide), when heated in a perfect vacuum or in an inert atmosphere, if the hypothesis under consideration is tenable. This begins even in the air at about 1000°. The search in chemical literature revealed a statement by Hilditch that cupric oxide ignited at lower temperatures in a vacuum weighs less than it did before, as well as one by Morley that the same substance slowly evolves a gas when heated in a vacuum (Hilditch, Chem. News, 1884, vol. xlix., 37; Morley, *Am. Journ. Sci.*, 1891, xli., 231). Since it is hard to tell whether this evolution might not be merely that of the occluded gases, it was thought worth while to repeat the experiment.

Two grms. of cupric oxide, which had been ignited for a long time in pure air until constant in weight, were found to evolve a gas steadily when heated in a vacuum to about the melting-point of common salt (790°), provided that the gas was removed by a Sprengel pump as fast as it was formed. When allowed to attain equilibrium, this gas (which repeated analysis showed to be almost pure oxygen, containing only traces of nitrogen and carbon dioxide) was found to possess a tension of two- or three-tenths of a m.m. of mercury. A portion of the same material was heated for many hours more in a crucible to a full red heat; but upon subsequently heating it in a vacuum the evolution of gas proceeded just as before. Since all the occluded oxygen except 2 or 3 per cent had been expelled by the preliminary heating, this must have been structural oxygen. The conclusion was confirmed by the discovery of red cuprous oxide in the residue. Repetitions of the experiment showed that the tension of the gas increased enormously with the temperature, exceeding a m.m. before the glass became so soft as to collapse. In some of the experiments the best Bohemian glass was used, in others the hardest made in Jena, The nature of the glass seemed to be without influence on the result. The amount of gas evolved in a given time naturally depends upon the efficiency of the pump, as well as upon the temperature; in one of the experiments 2 c.c. of oxygen were obtained in eight hours.

Ignition of the substance in an inert atmosphere should produce the same effect. Since cupric oxide is slightly dissociated by heat, perceptible amounts of oxygen should be removed by heating it in nitrogen, just as carbonic acid is removed from limestone by heating it in a current of air. This dissociation of cupric oxide must have its effect on any process involving the ignition of cupric oxide in a vacuum or in an inert gas. The determination of organic nitrogen by means of the Sprengel pump, for example, must be affected by it. The use of carbon dioxide as a displacing medium in the Dumas method probably disposes of the error, however; for carbon dioxide is itself dissociated by heat, and it undoubtedly furnishes enough oxygen to diminish greatly the decomposition of the cupric oxide.

In the light of these results it is obviously advisable, when one desires to remove oxygen from a mixture of gases by means of hot copper, to maintain the last portion of the tube at a comparatively low temperature. Even then the issuing gas may not be absolutely free from oxygen.

Everyone knows that auric oxide is excessively unstable, and that argentic oxide is completely decomposed even in an atmosphere of pure oxygen at comparatively low temperatures. The present results merely extend this behaviour, in a much smaller degree, to cupric oxide, and the hypothesis carries the idea still further. The dissociation of zincic oxide must of course be yet less, while the tension of oxygen above magnesic oxide even at high temperatures must be an infinitesimal far less in value than the tension of the gas in the vacuum needed for the production of X-rays.

According to the phase rule and the law of mass action these reactions must take place in the gaseous phase,—the only one present of variable composition. As an example, the case of copper is given below:—

$$\underset{\text{Vapour.}}{4CuO} \rightleftharpoons \underset{\text{Vapour.}}{2Cu_2O} + \underset{\text{Gas.}}{O_2}$$

$$\uparrow\downarrow \qquad\qquad \uparrow\downarrow$$

$$\underset{\text{Solid.}}{4CuO} \qquad \underset{\text{Solid.}}{2Cu_2O}$$

The occluded oxygen is supposed to escape by the oscillation, backward and forward, of this heterogeneous reaction. The ability of the system to be first dissociated and then associated in another place where more oxygen is present presupposes, however, great internal activity in the substance of the hot solids; and this internal activity is the most interesting conclusion to be drawn from the phenomena under discussion.

In short, no matter what point of view one adopts, or what mechanical picture one forms of the reaction, the necessity of ascribing the rapid escape of the oxygen to internal re-arrangement seems to be inevitable.

Professor Morse, in another letter received since the foregoing was written, kindly tells me that, in the course of some admirable work upon the atomic weight of cadmium which he has just completed, he has had occasion to measure the gases occluded by cadmic oxide made from the nitrate. As one would expect, this oxide holds its occluded oxygen more firmly than copper, but less firmly than zinc. In fact, the behaviour of the substance, according to Professor Morse's description, probably accords well with the hypothesis under consideration. His interesting results will soon be in print, and will speak for themselves. The fact that Rogers and I found no gas in our cadmic oxide in 1892 is easily accounted for by the circumstance that we used a bright red heat in the ignition the oxide parting with both gases by the disintegration of its original structure, as the oxide of copper did with Scott. Since cadmium is volatile at high temperatures, however, it was natural that its dissociated oxide should have a wider opportunity of re-arrangement than in the case of copper; and hence the crystalline structure of the ignited oxide observed in 1892. Nickel, another metal whose oxide was investigated by Rogers, probably occupies its expected place near cadmium, as far as its oxide's capacity to retain oxygen is concerned. In some recent experiments in this laboratory, Cushman succeeded in partially decomposing nickelous oxide in a stream of nitrogen below 1200°. All these considerations are concordant with the hypothesis devised to explain the escape of occluded oxygen for metallic oxides.

The only point regarding this occlusion of gases left unexplained is the fact that in the experiments of Morse and Arbuckle the total amount of gas was in every case nearly the same, although the proportion of oxygen and nitrogen varied. This is a very interesting circumstance. The experimenters ignited their oxide to constant weight,—in other words, until two successive ignitions caused no appreciable change; but it does not follow from this that the evolution of gas had ceased,—one can only maintain that it had become so slow as to be inappreciable. Evidently, then, the question to be answered is, Why has the oxygen more difficulty in escaping when a small amount of nitrogen is present than when a large amount is present? The reason of this eccentricity may be because those specimens which contain the most gas are naturally the most porous and loosely held together, although usually formed in larger individual aggregations; and the freer atomic and molecular motion allowed by the looser structure permits the oxygen to leave more rapidly. Hence in each case the sum of the oxygen and nitrogen amounted

to about the same volume. This hypothesis within an hypothesis is rather too uncertain to deserve much emphasis, however.*

In the course of some of my old experiments on the impurities in cupric oxide, it became necessary to reduce the substance in a current of carbon monoxide. Referring to this work Dr. A. Scott, in the paper already cited (*Proc. Amer. Acad.*, xxvi., 563), expresses surprise at the existence of an admixture of hydrogen in this gas. His experience agrees with that of Stas in finding only a small amount of such gaseous impurity in carbonic oxide obtained from oxalic acid, while my results indicated a large amount. Lord Rayleigh, in the course of his recent work on the density of gases (*Proc. Roy. Soc.*, 1898, lxii., 204), concludes that his carbonic oxide also was free from hydrogen or hydrocarbons; and indeed there is no reason why this result should not be easily attained if one uses pure materials. Lord Rayleigh explains the existence of hydrogen in my carbonic oxide by drawing attention to the fact that in my case the gas, dried only by calcic chloride, was passed over red-hot platinum sponge.

This explanation is undoubtedly correct. Many experimenters have shown that the reaction—

$$CO + H_2O = H_2 + CO_2$$

is an easily reversible one at high temperatures (Bunsen, *Liebig's Annalen*, 1853, lxxxv., 137; Horstmann, *Ibid.*, 1878, cxc., 228; Bötsch, *Ibid.*, ccx., 207; and especially Hoitsema, *Zeitschr. Phys. Chem.*, xxv,, 688, as well as others), and in the presence of a large excess of carbon monoxide, it is obvious that nearly all of the trace of aqueous vapour would be reduced. For my purpose at the time, the source of the hydrogen was of no importance; it was only necessary to know the exact amount of the impurity, and this was suitably determined. It is satisfactory to know the cause of the discrepancy, however, as well as to know that it is easier to prepare carbon monoxide almost free from hydrogen than seriously contaminated with it. More often than we suspect, perhaps, are our carelessly planned efforts at purification apt thus to introduce more impurity than they eliminate.

In a recent number of the *Journal of the American Chemical Society* (March, 1898) F. R. M. Hitchcock has published a preliminary paper upon the occlusion of various gases by the oxides of metals, having apparently overlooked the Harvard investigations. It is satisfactory to see the phenomenon widely recognised; for an appreciation of this serious cause of possible constant error will result in the publication of fewer erroneous determinations of atomic weights than have appeared in the past. One should also bear in mind the fact that nitric acid is not by any means the only substance which is liable to leave appreciable contamination in material from which it has been expelled by heat. The number of such occlusions is far greater than most analysts imagine; this fact is not realised because the minute residues are often so hard to detect.

The evidence of this paper proves that in reality no discrepancy exists between the results of Scott, and Morse and Arbuckle, and those obtained at Harvard. The apparent disagreements were caused by the fact that the later experimenters investigated parts only of the wide field outlined in 1892, the relation of the parts to the whole being partially unperceived. The paper also shows that the unequal escape of oxygen and nitrogen imprisoned in the oxides of metals is a phenomenon of great interest, capable of shedding light on the internal kinetics of solids.

* In this connection it is a matter of interest to note that Ramsay (*Phil. Mag.*, 1894 [5], xxxviii., 206) has found that the presence of nitrogen in a palladium bulb seems to prevent to some extent the diffusion of hydrogen into it. This observation is not unlike Morse and Arbuckle's; but if, as a matter of fact, an indifferent gas can produce such an effect, our present notions concerning semi-permeable septa demand some revision.

NOTICES OF BOOKS.

Text-book of Zoology. By H. G. WELLS, B.Sc. Lond., F.Z.S., F.C.P., and A. M. DAVIES, B.Sc. Lond. The University Tutorial Series. London: W. B. Clive, University Correspondence College Press. Pp. 366.

THIS book, though in one way a second edition of Wells's "Text-book of Biology" under another title, has, as a matter of fact, been almost entirely re-written; only one chapter (Chap. XIV.) remains practically the same as in the first edition.

The first twelve chapters are on the rabbit, its digestion, circulation, respiration, tissues, nervous system, reproduction, &c., being in turn all fully described and illustrated.

In Part II. the lower Vertebrata are similarly dealt with; among these we find the frog, the dog-fish, the lancelet, &c.: this part comprises four chapters.

In Part III., in six chapters, we have the development of the Vertebrata, such as the chicken and the rabbit; while in Part IV., consisting of five chapters, the Invertebrata are discussed: these include the slipper-animalcule, the fresh-water polype, the earthworm and crayfish.

At the end of each Part are a number of questions on the particular subjects just gone through. The whole book is arranged with regard to the preliminary and intermediate Science Examinations of the London University.

Photographic Formulæ. ("Ricettario Fotographico"). By Dr. LUIGI SASSI. Second Edition, Revised and Enlarged, with New Formulæ and Processes. Milan: Ulrico Hoepli. 1899. Pp. 167.

THE first part of this handy little volume describes the obtaining of negatives, their development, toning, fixing, &c., with 112 formulæ. Part II. deals with positive processes, and gives over 95 formulæ; while Part III., and last, consists of miscellaneous methods and items, all of considerable interest to photographers.

The book is primarily intended for the use of amateurs rather than professionals.

Aluminium. ("L'Alluminio"). By Dr. C. FORMENTI. With 67 Figures and 21 Tables. Milan: Ulrico Hoepli 1899. Pp. 323.

THE principal scope of this manual is to fully describe, in a practical and complete manner, the history, minerals, methods of production, properties, uses, commercial value, &c., of this comparatively new metal, aluminium. This is the first work on this subject published in Italy, and the author hopes, as he has good reason to, that it will compare favourably with those published in other countries. The printing, paper, and diagrams leave nothing to be desired.

The Galvanic Deposition of Nickel, Silver, Gold, Copper, &c. ("Galvanostegia, Nickelatura, Argentatura, Daratura, Ramatura"). By I. GHERSI. With Four Illustrations. Milan: Ulrico Hoepli. 1899. Pp. 323.

AS its title shows, this book deals solely with the electrodeposition of metals, and includes not only the more well-known ones, but also those which—like palladium, iridium, chromium, molybdenum, aluminium, cadmium, &c.—are less frequently met with. In the Appendix a number of special and experimental baths are described.

Colouring and Decoration by means of Metals, both by Chemical and Electrical Methods. ("Colorazione e Decorazione dei Metalli, per via Chimica ed Elettrica"). By I. GHERSI. Milan: Ulrico Hoepli. 1899. Pp. 190.

THE methods of obtaining decorative and coloured effects herein described cover a large field, and have abundant

applications in modern decorative art. Such processes as are described cannot be adequately illustrated in a book of this size, but the descriptions are full, and should be of great service to those interested in this branch of art.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 26, December 26, 1898.

Separation and Estimation of the Halogen Elements in their Silver Compounds.—H. Baubigny.—The author has devised a convenient method of analysing accurately a mixture of silver chloride, bromide, and iodide. He employs an oxidising agent in the presence of an acid, and finds the best results are obtained by using sulphuric acid and potassium bichromate, giving free chromic acid. At ordinary temperatures, the iodide and bromide are transformed into iodate and bromate. The solution of iodate can be filtered off and the iodine and bromine together estimated by the ordinary methods. If the original mixture is heated over a water-bath to 90° or 95°, bromine and chlorine are liberated, the iodate alone remaining unaltered. This can be filtered off and the iodine estimated.

Action of Oxidising Agents on certain Fatty and Aromatic Amines.—Œschner de Coninck and A. Combe.—The action of chromic acid and potassium bichromate in concentrated aqueous solution on the chlorhydrates of methylamine and ethylamine was investigated. Decomposition slowly took place under certain conditions with evolution of CO_2, Cl, and N. Analysis of the gases by the usual methods points to the following equations for the two cases:—1. $CH_3NH_2.HCl+5O = N+3H_2O+CO_2+Cl$; 2. $C_2H_5NH_2.HCl+8O = N+2CO_2+4H_2O+Cl$. The oxidation of several aromatic amines was also effected, with the result that pure CO_2 was evolved. The conclusions drawn are that, in the presence of energetic oxidising agents fatty amines decompose gradually, whilst aromatic amines are decomposed rapidly, with production of CO_2, their nitrogen remaining in combination in the molecule of coloured derivatives which arise.

Thermal Investigation of Normal Propylmalonic Acid. Heat of Formation of the Potassium Salt in the Solid State.—G. Massol.—The acid was prepared synthetically by the action of normal propyl iodide on the sodio-malonic ester, and purified by crystallisation from ether. Melting-point, 93·5°. The following points are enumerated:—I. heat of solution in water. II. Heat of neutralisation by potash in aqueous solution. III. Heat of formation of the solid neutral potassium salt.

$$\underset{\text{Solid.}}{C_6H_{10}O_4}+2KOH=\underset{\text{Solid.}}{C_6H_8O_4K_2}+2H_2O+46{\cdot}34 \text{ calories.}$$

Oxidation Products of Oxygluconic Acid.—Léon Boutroux.—The acid was oxidised by nitric acid under conditions favourable to the production of saccharic acid. The result was the production of four acids, viz.:—

COOH	COOH	CH_3	CH_2OH
HO.Ċ.H	H.Ċ.OH	H.Ċ.OH	ĊOOH
H.C.OH	HO.C.H	OH.Ċ.H	
HO.C.H	ĊOOH	ĊOOH	
ĊOOH			
Trioxyglutaric acid.	Racemic acid.	Dioxybutyric acid.	Oxyacetic acid.

which establishes the formula of oxygluconic acid as—

$$CH_2.OH.CO.\overset{OH}{C}-\overset{H}{C}-\overset{OH}{C}.COOH.$$

Journal de Pharmacie et de Chimie, Series 6, Vol. viii., No. 5.

Modification of Mörner and Sjoqwist's Method for the Estimation of the Nitrogen in Urea, or of Urea itself.—H. Moreigne.—The Mörner-Sjoqwist method, which consists in precipitating the nitrogenous principles of urine, other than urea, by adding chloride of barium, baryta, and a mixture of alcohol and ether, is one of the best we possess; but, as described, it can only be employed for certain scientific researches. The author has modified this method, making it more simple and more practical, by suppressing Kjeldahl's operation and estimating the nitrogen of the urea (which is in the residue after evaporation) in the ureometer by means of an alkaline solution of hypobromite of soda.

Volumetric Estimation of the Nitrogen in Urea, or of Urea, by means of an Alkaline Solution of Hypobromite of Soda after Treating the Urine—1st with Phosphotungstic Acid, 2nd with Basic Acetate of Lead and Phosphotungstic Acid.—H. Moreigne.—Normal urine treated with sub-acetate of lead, as is generally done by ureologists, still contains ammoniacal salts, creatinine, and guanine. The latter may be neglected, but it is different with the salts which give up all their nitrogen, and with creatinine which gives up half; thus the nitrogen is considerably augmented, the ammoniacal salts supplying one-eighth or one-tenth of the total. The author has for some years advocated the use of phosphotungstic acid instead of sub-acetate of lead, but now, after having had more experience, he recommends a process in which the basic acetate of lead and phosphotungstic acid are used successively. This method will be fully described in the continuation of the paper.

Microscopic Examination of Wheaten Flours.—E. Colin.—Not suitable for abstraction.

The Direct Synthesis of Anisol and Phenethol.—Ch. Moureau.—A classic method for the preparation of phenols consists in melting the sodium or potassium salts of the sulpho-derivatives of the benzenic hydrocarbides with potash or soda,—

$$\underset{\text{Benzino-sulphonate of sodium.}}{C_6H_5.SO_3Na}+NaHO=SO_3NaO_2+\underset{\text{Phenol.}}{C_6H_5OH}.$$

If, in the above equation, the soda is replaced by methylate of sodium, $NaOCH_3$, we have a new equation, a methyl grouping replacing the hydrogen of the soda—

$$C_6H_5.SO_3Na+NaOCH_3=SO_3Na_2+C_6H_5.OCH_3.$$

The author thought this reaction might take place in such a way as to furnish anisol by direct synthesis, and experiment has confirmed his expectations. The materials used must be perfectly dry. The mixture of phenylsulphonate of sodium and methylate of sodium in equal molecules is distilled on an oil-bath up to a temperature of 350°, when an oily liquid comes over; this is washed with dilute soda and dried over chloride of calcium. It boils at 152—154°. Analysis shows it to have the composition of anisol. If the methylate of sodium is replaced by ethylate of sodium, phenethol ($C_6H_5.OC_2H_5$) is formed; it is an oily colourless liquid boiling at 168—171°.

The Decomposition of Iodoform in Solution.—J. Bougault.—Two grms. of iodoform, 30 c.c. of ether, and 30 c.c. of a 1 per cent solution of hyposulphite of soda are placed in a flask of about 90 c.c. capacity, the flask is sealed hermetically and exposed to direct sunlight. The solution of iodoform undergoes a rapid partial decomposition; agitate to absorb the iodine, and a further decomposition takes place after a certain time, depending on how often the flask has been shaken. We notice that the ethereal solution of iodoform no longer takes a brown colour, and is no longer decomposed by light; it can now be kept for months without further appreciable decomposition; but if the flask be opened, and a fresh supply of oxygen (air) be allowed to enter, the decomposition recommences at once. The experiment, says the author,

proves that oxygen intervenes in the decomposition of solutions of iodoform exposed to light. The solution of hyposulphite of soda can be replaced by any other substance which absorbs iodine and which has no action on iodoform, such as mercury or finely-divided silver.

The Reagents for Cotton Seed Oil.—Kiamil Mazar.—Comparative experiments on over 300 samples of oils lead the author to the conclusion that nitric acid (5 c.c. of oil and 10 c.c. of acid at 1·40 free from nitrogen) gives uncertain results. Hirschsohn's reagent (5 c.c. of oil and 10 drops of a chloroformic solution of chloride of gold at 0·5 per cent) is not sensitive. Becchi's reagent (5 c.c. of oil and 25 c.c. of absolute alcohol, and 5 c.c. of a 1 per cent solution of nitrate of silver in absolute alcohol) gives doubtful results. He only finds Halphen's reagent satisfactory, which consists in using equal parts of oil, amylic alcohol, and sulphide of carbon saturated with sulphur.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—G. C. Cathcart, Hon. Alan de Tatton Egerton, M.P., Sir Francis Henry Evans, K.C.M.G., M.P., J. G. Glover, J. W. Gordon, J. Gretton, J. Gretton, jun., M.P., C. E. Groves, F.R.S., and A. Ritchie, J.P. The special thanks of the Members were returned to Professor Dewar for his donation of £100, and to Mr. Frank Clowes for his donation of £10 10s. to the fund for the promotion of Experimental Research at Low Temperatures. The special thanks of the Members were returned to Mr. C. E. Melchers for his donation of £50 for alterations in the Lecture Theatre.

The Late Duke of Northumberland and the Royal Institution—At the General Monthly Meeting of the Members of the Royal Institution, held on February 6th, the following resolution was proposed from the chair by Sir James Crichton-Browne, M.D., F.R.S., the Treasurer, seconded by Sir Frederick Bramwell, F.R.S., the Honorary Secretary, and unanimously adopted:—"The Members of the Royal Institution of Great Britain in General Meeting assembled desire to express to his Grace the Duke of Northumberland their sympathy with him and his family in the loss which they, as well as the Royal Institution and the country at large, have sustained by the death of his father, the late Duke. They desire also to record their grateful sense of the invaluable services rendered to the Royal Institution by the late Duke during his membership of 48 years' duration, during seven terms of office as Visitor and Manager, and as President for 26 years, by his active and unfailing interest in its affairs, and in the progress of science, which it is its object to promote; by his generous benefactions to its funds, and by the true nobility of his character, which has lent distinction to its proceedings during an eventful period of its history."

Merck's "Digest."—We have received No. 1 of this new periodical, which is to consist of a selection of reports on new chemicals and drugs, taken from the latest medical, pharmaceutical, and other scientific literature. The first number is devoted to the description of the glycerino- or glycerophosphates and their applications. Glycerophosphoric acid, $H_2PO_4C_3H_5(OH)_2$+aq., is a pale yellow, oily, odourless liquid, having a sour taste; it is soluble in water and alcohol; its natural source is a decomposition product formed during digestion. Lecethin, the chief phosphorus constituent of food, is decomposed in its passage through the system into choline and glycerophosphoric acid; the latter is the form in which phosphorus is assimilated. The acid is not used medicinally by itself, but in the form of salts of ammonium, calcium, iron, potassium, quinine, &c. Physiologically phosphoglyceric acid possesses an elective action upon the nutrition of the nerves, and is said to be beneficial in cases of sciatica, neurasthenia, convalescence from influenza, and acute febrile affections, &c. It may be administered either internally or as a subcutaneous injection.

The Theory of Incandescent Gas-Lighting.—M. Drossbach.—According to the author the light given by an Auer mantle is due to the influence exercised by the molecule of oxide of cerium. This influence consists in bringing the calorific vibrations of the thorina into harmony with the calorific waves of the flame, which are then transformed into luminous waves. The author has prepared nitrates of thorium and cerium as pure as possible, and he found that the maximum illuminating power was given by a mantle containing 99·1 per cent of oxide of thorium, and 0·9 per cent of oxide of cerium. The substitution of zirconium for thorium gives bad results. He concludes that oxide of cerium does not possess any chemical or catalytic action. It has been stated that thorina prepared from the nitrate is always very voluminous, and that the great surface it offers to the flame favours the catalytic action of the oxide of cerium. Now the author shows that the sulphate, which makes a compact oxide, gives as good results as the nitrate.—*Journ. für Gasbeleuchtung*, xli., p. 352.

MEETINGS FOR THE WEEK.

TUESDAY, 14th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

WEDNESDAY, 15th.—Society of Arts, 8. "The Balloon as an Instrument of Scientific Research," by the Rev. J. M. Bacon, F.R.A.S.

—— Institution of Mining and Metallurgy, 8. "Notes on Dry Crushing on the Witwatersrand," by F. White. "Notes on Economical Mining at Myall's United Gold Mine, New South Wales," by W. R. Thomas. "Mica Mining in Bengal, India," by A. M. Smith.

—— Microscopical, 7.30. Exhibition of Objects shown by Multiple Colour-illumination, by J. Rheinberg.

THURSDAY, 16th.—Royal Institution, 3. "Toxins and Antitoxins," by Dr. Allan Macfadyen, M.R.C.S.

—— Chemical, 8. "On the Absorption-spectrum and Constitution attributed to Cyanuric Acid," by W. N. Hartley, F.R.S. Ballot for the Election of Fellows.

FRIDAY, 17th.—Royal Institution, 9. "George the Third as a Collector," by R. R. Holmes, M.V.O., F.S.A.

SATURDAY, 18th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

A leading Company in the North of Ireland, engaged in the Linen Trade, desire to secure the services of a scientific Chemist, to study the processes and analyse the chemicals employed in their Bleach Works.—Apply, stating age, qualifications, and salary expected, to "Bleachers," Chemical News Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, Chief Chemist and Manager of Works by a leading London firm of Manufacturing Chemists employing several hundred people. The qualifications necessary for the position are high and well grounded scientific knowledge and attainments, good practical experience in carrying out manufacturing processes, exceptional powers of organisation and administration, tact, good judgment, capability to direct and control scientific workers engaged in the manufacture of fine Medicinal Chemicals and Pharmaceutical Products. A gentleman with University Training and Degrees preferred. The position commands a liberal salary. Replies will be treated in the strictest confidence if so desired.—Address, stating age, qualifications, and experience, to "Manager," care of Messrs. Markby, Stewart, and Co., 57, Coleman Street, London.

Wanted, berth as Assistant to an Analyst, either in a Public or Private Laboratory, preferably with a Fellow of the Institute of Chemistry. A year's experience in a Public Analyst's Laboratory; two years in a Chemical Laboratory. Member of the Pharmaceutical Society.—Address, J. S. Turner, 20, Bury Street, London, W.C.

THE CHEMICAL NEWS.

Vol. LXXIX., No. 2047.

APPLICATION OF LIQUID HYDROGEN TO THE PRODUCTION OF HIGH VACUA, TOGETHER WITH THEIR SPECTROSCOPIC EXAMINATION.*

By JAMES DEWAR, M.A., LL.D., F.R.S.

As an illustration of the extraordinary power of the new cooling agent—liquid hydrogen,—the extreme rapidity with which high vacua can be produced by its use is perhaps one of the most striking. The absolute boiling-points of hydrogen, oxygen, and chlorine are respectively 35°, 90°, and 240°; in other words, oxygen boils at a temperature two and a half times higher than liquid hydrogen, and liquid chlorine similarly two and a half times that of liquid oxygen. From this we infer that liquid hydrogen as a cooling agent ought to be relative to liquid air as effective as the latter is compared to that of liquid chlorine. Now chlorine at the temperature of boiling oxygen is a hard solid, some 80° below its melting-point, and in this condition has an excessively feeble vapour pressure. When liquid hydrogen freezes air out of a sealed tube by immersing the end in the liquid, it is to be inferred that no measurable pressure of air ought to be left in the vessel. If we apply Van der Waal's law of corresponding temperatures to the case of hydrogen, the above inference is made unimpeachable. An approach to some knowledge of what the tension of air must be about the boiling-point of hydrogen can be attained by exterpolating the vapour-pressure curves of oxygen and nitrogen. Taking the following range of boiling-point temperatures for nitrogen and oxygen, viz., from the critical-point to the boiling-point under diminished pressure, two Willard Gibbs formulæ were calculated, with the following results :—

Nitrogen	Temp. abs.	127°	78·6°	59°
	Pressure in m.m..	25,900	740	26

Nitrogen. $\log_{10} p = 11{\cdot}5561 - \frac{400{\cdot}02}{T} - 1{\cdot}8980 \log_{10} T$ . . 1.

Oxygen	Temp. abs.	154°	90·3°	61·3°
	Pressure in m.m..	37,592	740	7·5

Oxygen. $\log_{10} p = 9{\cdot}4699 - \frac{422{\cdot}22}{T} - 0{\cdot}9843 \log_{10} T$ . . 2.

Another Gibbs formula was calculated, taking Estreicher's values for the vapour-pressure of liquid oxygen below its boiling-point, viz. :—

Temp. abs.	91·44°	78·1°	62·8°
Pressure in m.m..	743·8	141·8	7·5

Oxygen. $\log_{10} p = 16{\cdot}0670 - \frac{524{\cdot}72}{T} - 3{\cdot}8024 \log_{10} T$ . . 3.

We deduce from these formulæ the following vapour-pressures at the temperature of boiling hydrogen :—

1. Nitrogen ..	0·0015	Pressure in m.m., 35° abs.
2. Oxygen ..	0·000076	do.
3. ,, ..	0·000016	do.

The results of calculation, taking the formulæ for the widest range of pressures, viz., 1 and 2, may probably be the surest, but in any case those values must be taken as a *maximum*, seeing they refer to the liquid state, while both oxygen and nitrogen at the temperature of 35° absolute, are hard solids, and must therefore have dropped to lower tensions than that of the exterpolated liquid vapour-pressure curves. It is curious to note that at this low temperature the theoretical ratio of the tensions of nitrogen and oxygen is as 20 to 1. Direct measurements of

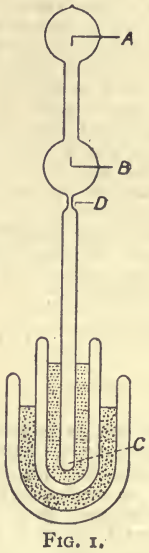


Fig. 1.

Fig. 2.

the vapour pressure of nitrogen at the melting-point, or 60° absolute, gave the value of 26 m.m., and a ratio of the tensions of nitrogen to oxygen of 6 to 1, whereas from the curves the value ought to be 6·7 to 1. Olszewski gives

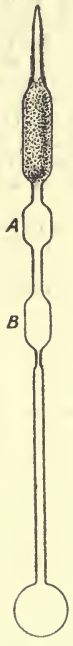


Fig. 3.

the tension of nitrogen at −214° as 60 m.m., and as at this temperature the oxygen tension is 3·8 m.m., the ratio of the saturated pressures of the two gases at the melting-point of nitrogen would be as 16 to 1, which is far too high. Probably the oxygen value will be nearest the

* A Paper read before the Royal Society, December 15, 1898.

truth, seeing it has the lowest melting-point. The tension is about a ten-millionth of an atmosphere. In the case of nitrogen, the maximum theoretical pressure would be one five-hundred-thousandth of an atmosphere. It is safe to infer that the vacuum left after liquefying the air out of a vessel by means of liquid hydrogen cannot exceed the millionth part of the atmospheric pressure, exclusive of the pressure resulting from any incondensable material other than nitrogen and oxygen. This is just about the pressure of the vapour of mercury at the ordinary temperature in the Torricellian vacuum, so that as good an exhaustion ought to result as can be got by boiling out a space with mercury. There is another way in which the question may be put. Assuming the molecular latent heats are approximately proportional to the absolute boiling-points, then we can, from a comparison with the oxygen value, deduce that of hydrogen, and thereby get the constants in a two term formula for the vapour-pressures. For pressures below an atmosphere, the following approximate formulæ were deduced:—

Oxygen .. $\log p = 7{\cdot}2058 - \frac{392{\cdot}6}{T}$ m.m. . . . 4.

Hydrogen $\log p = 7{\cdot}2428 - \frac{152{\cdot}7}{T}$ m.m. . . . 5.

From these expressions it follows that at its boiling-point, or 35° absolute, hydrogen has 7/852000 times the pressure of oxygen, or the latter pressure is about the eight-millionth of an atmosphere. A similar formula, calculated from the critical- and boiling-point data, gives substantially the same order of quantities. Formula 4 for oxygen tensions must be fairly accurate, seeing it gives a theoretical latent heat of about 56 units per grm. of liquid evaporating at the boiling-point, whereas direct determinations result in 55 units. To test this inference, the following plan of experimenting was adopted:—Ordinary shaped vacuum tubes, like A, B, used for the spectroscopic examination of gases, with and without electrodes (Figs. 1 and 2), having a capacity ranging from 15 to 25 c.c., had pieces of quill tubing about a foot long sealed on. The tubes were contracted at D to about 1 m.m., so that they could be sealed off with rapidity. The end C sometimes terminated in a small bulb (Fig. 3), in order to give increased cooling surface, and, when necessary, to allow many times the volume of air in A B to enter and be condensed with the object of accumulating any incondensable residuum.

The tubes were filled with air, oxygen, and nitrogen at the atmospheric pressure. The liquid hydrogen collected in the vacuum vessel, immersed in another similar vessel full of liquid air, being ready, the end C was dipped in the liquid for a little over a minute, and the tube A B sealed off at D, so that on removal from the hydrogen bath the solid air might melt and distil off wihout generating any pressure. On attempting to pass the spark through vacuum tubes prepared in this manner, their excellent exhaustion was revealed by great resistance to the passage of the discharge, and the high phosphorescence of the glass. Two tubes, kindly prepared by Sir William Crookes with platinum electrodes that he had previously sparked to remove gases and impurities on the glass before filling with dry air, gave, when treated in the manner described, such high vacua that the tubes had to be heated in order to get any spark to pass. Thus, it is proved that the tension of solid nitrogen and oxygen at the temperature of boiling hydrogen is below the millionth of an atmosphere, seeing there is less difficulty in getting a discharge to pass in tubes exhausted to this extent. In order to get some definite idea of the limit of the exhaustion produced, two tubes, such as have been described as suitable for the liquid hydrogen experiments, might be joined together and filled with oxygen or nitrogen at atmospheric pressure, and simultaneously exhausted with the mercurial pump to a small fraction of an atmosphere, and then sealed off from the pump and each other. One of these two identical tubes could then be subjected to the hydrogen cooling, following the directions already given, and the two vacuum tubes now compared. If there was a marked difference in resistance to the passage of the discharge in the frozen tube, then something must have condensed, and by a few tentative trials a limit might be reached when the initial exhaustion was unaffected by the hydrogen cooling. Such experiments have not yet been made. The presence of any vapour of mercury would require to be carefully eliminated, otherwise the method would not be satisfactory. Tubes that are prepared without taking special precautions to exclude organic matter and water from the glass, deteriorate, especially with electrodeless tubes after the discharge has taken place for some time.

The rapidity with which the vacua are attained is such as theory would suggest, assuming a hole of a square millimetre in section through which the air rushes into the condenser and that a velocity of current between 600 and 700 feet a second is attained, then a vessel of 20 c.c. capacity could be reduced in pressure in one second to 1/10 of the initial pressure, and if the same rate is continued at the end of sixty seconds to $(\frac{1}{10})^{60}$. Sir George Stokes has been good enough to consider the problem, and writes as follows:—

"Let V be the volume of the vessel, A the area of an aperture by which the air is conceived as rushing out with the velocity v, ρ the density of the air in the vessel at the time t, D the initial density—that is, the atmospheric density.

"Then, according to our hypothesis, $Av.dt$ is the volume of air, and, therefore, $Av\rho.dt$, the mass of air, which rushes out in the time dt. But this equals the loss of mass of air in the vessel during the time dt, and, therefore,—

$$Av\rho \,.\, dt = -V d\rho,$$

a differential equation of which the integral is—

$$\rho = De^{-Avt/V}.$$

"Suppose now V to be 20 c.c., or 20,000 c.m.m., A to be the area of a circle of 1 or 2 m.m. diameter—say 2 sq. m.m., v to be 333 m., or 333,000 m.m., t (in seconds) to be 60; then—

$$\log_e \frac{D}{\rho} = \frac{2 \times 333{,}000 \times 60}{20{,}000} = 1998,$$

$$\frac{D}{\rho} = 5254 \times 10^{434}.$$

"This would give a density of almost inconceivable smallness. Doubtless the supposition made above as to the rate of discharge is very wide of the mark, being much too great. If the velocity of rushing is about half the velocity of sound, the ratio of densities would become 72×10^{217}. If so, it is satisfactory to find that the mathematical following out of the hypothesis leads to a density of the residual air in the vessel which is enormously below what suffices to account for the observed result." A practical mode of rapidly attaining a high vacuum in any vessel is to displace the air with carbonic or sulphurous acid, either at the atmospheric or under diminished pressure, and then to freeze out the remaining gas by the use of liquid air, just as in the experiments with liquid hydrogen.

The first vacuum tube was an electrodeless one, the air had not been dried, nor the glass specially cleaned. On spectroscopic examination it showed hydrogen lines bright along with the second or compound line spectrum of the same gas, and a series of bright bands defined on the less refrangible side, diffuse on the more refrangible, which occur in the yellow, green, blue, and indigo. These bands were found to be identical with the carbonic oxide spectrum. With a Leyden jar in the secondary circuit the line spectrum of hydrogen disappeared, leaving the second spectrum fainter; but the carbonic oxide bands remained bright, and there was no appearance of the hydrocarbon

spectrum. The second tube had aluminium electrodes, and, like the last, had no special treatment in filling in the air. This tube showed also the line spectrum and the second spectrum of hydrogen; the latter being bright along with the carbonic oxide spectrum; but on sparking the latter disappeared. No appearance of the hydrocarbon spectrum could be detected, but there was a suspicion of bands in the indigo like the negative pole spectrum of nitrogen. The addition of a Leyden jar brought out nothing new, only intensifying the line spectrum of hydrogen, while leaving the second spectrum bright. In neither of the above tubes could any lines of nitrogen or oxygen be recognised. The third tube was filled with air drawn over cotton-wool, red-hot copper oxide, and phosphoric pentoxide, no rubber joints being employed. The spectrum showed the carbonic oxide bands and the hydrogen line spectrum as before. Only the second hydrogen spectrum was feeble. There was a yellow line, W. L. 5849, identical with one occurring in the natural gas from the King's Well at Bath. In a paper on "The Liquefaction of Air and the Detection of Impurities" (*Chem. Soc. Proc.*, November, 1897), the separation of helium from this gas is described by liquefaction and fractionation, and it was observed that during the sparking the helium lines were well marked along with "*others, the origin of which must be settled later.*" It was further observed, "*With a modified form of apparatus it will be possible to collect any residuary gas from the use not of 3 cubic feet of air or Bath gas, but from hundreds of cubic feet of such products.*" The helium and other associated material was shown to be more volatile than nitrogen. Pursuing this course of investigation in the summer of this year, the volatile portion of air was examined, when the presence of material giving the same lines as Bath helium was recognised. While this investigation was in progress, Professor Ramsay and Dr. Travers observed the same spectrum in the more volatile portion of argon which they have associated with a new element called neon. The use of liquid hydrogen, as described, proves that the most characteristic line of neon in the yellow, about W. L. 5849, can be detected in 25 c.c. of ordinary air, and the presence of helium in the atmosphere is confirmed.*

A fourth tube, filled like the preceding one, had a phosphoric pentoxide tube left on. This showed again the carbonic oxide bands, but no hydrogen lines could be detected; while the oxide of copper ought to have removed all free hydrogen and transformed all the organic matter into carbonic acid and water. Yet it appears that the spectrum of the carbon compounds is difficult to remove from electrodeless tubes, probably owing to carbonic acid coming from the glass. There were some broad diffuse bands that may arise from the drying agent. The absence of hydrogen in this tube suggests that its presence in the third tube was due to vapour of water coming slowly from the glass. I am greatly indebted to Professor Liveing for making a careful examination of the spectra of these tubes.

Sir William Crookes was good enough to prepare two tubes with platinum electrodes, which he sparked in vacua till all hydrogen disappeared, and then filled with dry air, but without the use of red-hot copper oxide or any agent for the absorption of carbonic acid or the destruction of organic matter. After the cooling with liquid hydrogen, he found on spectroscopic examination, in one no hydrogen, but two faint lines, one about 5852 W.L. and the other 5676 W.L. The second tube showed the same yellow about 5852, the helium line along with 5939 and 6145, the hydrogen lines C and F, and some red lines. The observations of Crookes confirm the presence of neon, helium, and hydrogen. The absence in his tubes of the carbonic oxide spectrum is important, seeing all the electrodeless tubes gave this spectrum. In these tubes the vacuum was very high, and it was difficult to observe the gaseous spectrum. Still, the fact of finding hydrogen in one and not in the other leaves the presence of free hydrogen in the atmosphere as a question for further inquiry. The tube that did not contain hydrogen was heated very hot in order to get a discharge, and then the spectrum showed some bands like the negative glow of nitrogen. Occasionally a jar discharge was got to pass, and when this took place the nitrogen lines could be seen. An electrodeless tube filled carefully with oxygen made from fused chlorate of potash, which was contained in an extension of the vacuum tube, gave nothing but the carbonic oxide bands. In future experiments it will be easy to concentrate all the least volatile material in air or other gases, and thereby to make a more thorough examination of the spectrum. In the meantime my object is to show one of the scientific uses of liquid hydrogen.

I have to thank Mr. Robert Lennox for efficient aid in the conduct of the difficult experiments. Mr. Heath has also helped in the work.

* In a paper along with Professor Liveing, "On the Spectrum of the Electric Discharge in Liquid Oxygen, Air, and Nitrogen" (*Phil. Mag.*, 1894), we noted that during the distillation and concentration *in vacuo* of liquid oxygen and air under diminished pressure that two bright lines appeared in the spectrum at wave-length 557 and 555, and that one of these lines was very near the position of the auronal line. These lines are now attributed by the same chemists to a new element, crypton.

DISPLACEMENT OF METALS BY MAGNESIUM.

By EDWARD G. BRYANT, B.Sc.

IT is stated in many text-books that magnesium will replace zinc, silver, lead, and copper, if added to solutions of the salts. This is quite true; but when exercises are set to students to determine the equivalents of these metals by means of magnesium, failure occurs, because in every case secondary actions are set up which result in the change of part of the magnesium or the other metal into oxides or basic compounds.

Clowes and Caven (*Journ. Chem. Soc.*, 1898) have shown this in the case of copper and magnesium. The following experiments were undertaken with the view of examining the action on the other metals mentioned above. The materials used were not *specially* purified; the experiments were made under the same conditions that laboratory students would have to work under.

1. *Magnesium and Zinc Sulphate.*—The following table shows that in every case, whether the solution be hot or cold, strong or weak, only a little more than 50 per cent of metallic zinc can be obtained. The first three results are certainly too high, and are due to all the magnesium not having disappeared. In the cold the action takes several days to complete, as judged by the gradual increase in the amount of gas generated. The residue always consisted of greyish metallic zinc and a considerable quantity of zinc and magnesium oxides. There was no sulphate present in the residue, and it had no effect on permanganate of potash. The amount of metallic zinc was estimated by measuring the hydrogen given off on dissolving the residue in dilute HCl. The gas given off during the reaction could be used as a check, as it measured the amount of oxidation of the two metals. Magnesium ribbon was used.

	Concentration of $ZnSO_4$.	Temperature.	Zinc reduced. Per cent.	
1.	5 per cent	13° C.	63	These are probably several per cent too high.
2.	10 ,,	13	66	
3.	10 ,,	60	65	
4.	20 ,,	70—80	55	
5.	5 ,,	13	60	
6.	2 ,,	5	56·8	
7.	20 ,,	13	54	

2. *Magnesium and Lead.*—Kirn (CHEM. NEWS, xxxii., 309) states that magnesium in lead nitrate is quickly covered with metallic lead, the lead soon changing into hydrate. I found that whether I used lead nitrate,

chloride (in hot solution), or acetate, and whether the solution was made slightly alkaline or not, that hydrogen was given off as well as lead reduced. In the case of lead chloride, the lead appeared as brilliant flakes, otherwise as a black powder.

As the gas came off very slowly at first, but increased when the solution was heated or after a certain amount of lead was deposited, the experiment was varied by dropping the solution on to the magnesium contained in a filter, just fast enough to keep the funnel about half full. No gas could be seen under these conditions, but after four hours there was still metallic magnesium left coated with lead, and only 50 per cent of the theoretical quantity of lead was obtained. I did not find that the lead oxidised under these conditions as long as it was covered with liquid; but when being dried it became perfectly white, and was estimated as PbO after ignition. The amount of magnesium used was from 20 to 50 m.grms. in fine powder.

3. *Magnesium and Silver.*—The action is very similar to that of lead, no gas being evolved at first, but the amount increasing as the experiment progresses or on heating. If any of the magnesium powder floats on the surface, a brilliant mirror of silver forms round it. The silver comes down in black flocculent masses, but on standing or washing with dilute acid turns to brownish crystalline particles. The table gives the results obtained; once the theoretical result occurred. From 20 to 50 m.grms. magnesium used.

Concentration of $AgNO_3$.	Temperature.	Amount of silver recovered. Per cent.	Remarks.
2 per cent	15° C.	66	Ribbon used, free Mg left in residue.
2 ,,	60	50	MgO in residue.
2 ,,	15	66	Ribbon; much metallic Mg in residue.
2 ,,	13	65	Result taken after two days; no free Mg, but much MgO in residue.
2 ,,	15	102	$AgNO_3$ dropped on Mg filings for 2 hrs. No gas evolved.
2 ,,	15	65 (twice)	Rather coarser filings than the last. No visible gas evolved.
2 ,,	15	112·2	Solution of $AgNO_3$ dropped for 4 hours on fine filings. No gas evolved.

I have never been able to account for the last result. There is a certain accordance about the others, which renders it probable that the theoretical result, or near it, might be obtained if sufficient precautions are used, but it cannot be described as an elementary exercise.

King's School, Pontefract,
February 4, 1899.

THE ACTION OF THE BACILLUS COLI AND EBERTH'S BACILLUS ON NITRATES.

By L. GRIMBERT.

I HAVE already shown that, contrary to the opinion of certain writers, the bacillus coli and Eberth's bacillus do not give off nitrogen when cultivated in a 1 per cent solution of nitrated peptone; but as, on the other hand, we get a disengagement of gas when the solution of peptone is replaced by a peptonised beef broth, it appeared to me to be interesting to try and find the cause of this different action, and to discover the origin of the nitrogen produced.

I therefore undertook a number of experiments in which I estimated the amount of gas given off, the nitrate destroyed, the nitrite remaining, and what I have termed the *amidised nitrogen*, that is to say the nitrogen furnished by the complex amidised materials in my culture media, before the intervention of any microbes, but when treated only by hypobromite of soda.

A. With the object of emphasizing the difference which exists between the action of bacilli on the nitrates and that of true denitrifying agents, I infected, on the one hand, a peptonised broth nitrate to 1 per cent with the bacillus coli and with Eberth's bacillus, and, on the other hand, a solution of nitrated peptone with the pyocyanic bacillus.

At the end of a month I obtained the following results:—

The pyocyanic bacillus gave off nitrogen only. The volume of nitrogen collected (100·48 c.c.) is equal to the nitrate destroyed (100·41 c.c.), and is seven or eight times greater than that of the amidised nitrogen (13·80 c.c.). The colon and typhoid bacilli give off nitrogen and carbonic acid. The volume of this nitrogen (28·09 c.c. and 26 96 c.c.) is practically the double of that which corresponds to the nitrate destroyed (12·34 c.c. and 13·0 c.c.), and much less than that of the amidised nitrogen from the culture (47·12 c.c.). Only one-half of the nitrogen is therefore furnished by the nitrate, the other half coming apparently from the amidised materials of the culture medium, on account of the reaction which takes place between these principles and the nitrous acid produced by the bacteria. This is the secondary phenomenon of a long known biological fact, viz., the reduction of nitrates by the bacilli of Eberth and Escherich.

B. If to a nitrated solution of peptone we add substances capable of losing their nitrogen by the action of nitrous acid, we ought to have a disengagement of gas; this is what takes place with extract of meat rich in waste nitrogenous matter, but only slightly nutrient in itself. The bacillus coli sown in a solution of peptone nitrated to 1 per cent does not give off any nitrogen. In a nitrated solution of meat extract without peptone it gave 7 c.c. at the end of a month, a volume corresponding to double that of the nitrate destroyed (2·9 c.c.), and in a 1 per cent solution of peptone, to which is added 1 per cent of meat extract and 1 per cent of potassic nitrate, we obtain, under the same conditions, 23·45 c.c. of nitrogen, the nitrogen corresponding to that which has disappeared being only 6·95 c.c.

C. With a 1 per cent solution of peptone giving 13·8 c.c. of amidised nitrogen, we can thus, by increasing the proportion of peptone, introduce into the solution an amount of amidised principles sufficient to cause a further disengagement of nitrogen. In fact, a 5 per cent solution of peptone containing 1 per cent of nitrate of potassium, and representing 71 c.c. of amidised nitrogen, gives, with the bacillus coli, 16·29 c.c. of nitrogen, and with Eberth's bacillus 11·29 c.c.; the amounts of nitrogen lost by the nitrate being respectively 8·7 c.c. and 2·9 c.c.

D. Contrary to certain opinions, the presence of nitrites does not stop the fermentation. The two bacilli develope very well in a peptonised solution of extract of meat containing 1 per cent of nitrite of potassium, and nitrogen is given off in a quantity equal to or even greater than that which they gave in the same medium when nitrated.

To sum up, whenever the bacillus coli or the bacillus of Eberth have caused a disengagement of gas in a nitrated medium, the volume of nitrogen collected has always been at least *double* that which corresponds to the nitrate destroyed. Consequently *the nitrogen given off does not come exclusively from the nitrates.*

The denitrifying action of these bacilli is correlative with the presence of amidised materials in the culture medium. It seems to be the result of the secondary action exercised on these latter by the *nitrous acid* produced by the bacteria.

Nitrites do not interfere with the action of these bacilli.—*Journ. de Pharm. et de Chim.*, Series 6, vol. ix., No. 2.

ON BECQUEREL'S RAYS AND POLONIUM.

By Madame S. CURIE.

The discovery of Becquerel's rays is due to the researches undertaken after the well-known discovery by Röntgen of the photographic effects of certain phosphorescent and fluorescent substances. These researches appear to throw a new light on a part of physical science. We now propose to discuss certain new facts and ideas that these facts give rise to in respect to natural philosophy.

Uranic Rays.

In an article by M. Poincaré which appeared recently in the *Revue Générale des Sciences*, the following remark appeared:—"The glass of a Crookes tube when bombarded by the cathode rays becomes fluorescent; this fluorescence is associated with the emission of Röntgen rays. We may, therefore, reasonably enquire if all bodies, of which the fluorescence is sufficiently intense, do not emit Röntgen rays as well as luminous rays, no matter what may be the cause of the fluorescence."*

Shortly afterwards M. Henry showed that phosphorescent sulphide of zinc could produce photographic impressions through a sheet of black paper quite impervious to light.

Niewenglowski observed the same phenomenon with sulphide of calcium which had been exposed to light. These observations may be better understood by admitting that the photographic effect was due to invisible rays, analogous to X-rays, that were emitted by the bodies in question.

Later on M. Troost obtained strong photographic impressions with an artificial phosphorescent hexagonal blende through black paper and thick cardboard.

M. Becquerel made similar experiments with uranium salts, some of which are fluorescent. He obtained photographic impressions through black paper with the double sulphate of uranium and potassium. He first thought that this salt, which is fluorescent, behaves like the sulphides of zinc and calcium, but further observations showed that this analogy did not really exist. It is true that uranium salts act on photographic plates through opaque bodies, but this action is in no way connected with fluorescence. Uranium and all its compounds, whether fluorescent or not, act in the same manner, and metallic uranium is the most active of them all. M. Becquerel also noticed that light is not necessary, but that uranium compounds kept in the dark for years continued to act on photographic plates. This was an entirely new phenomenon. He also showed that uranic rays were possessed of the following properties:—They traverse opaque bodies, but are absorbed more easily, and are therefore less penetrating than Röntgen rays. They make the air through which they pass a conductor of electricity, as do Röntgen rays; this is an important property of both kinds of rays.

Thoric Rays.

Following these results it was only natural to ask if uranium was the only metal possessed of this property, and M. Schmidt has found that compounds of thorium are the only ones endowed with similar properties. The activity of the oxides of these two metals is equal, and, approximately, their compounds are more active in proportion to the amount of the metal they contain.

Uranic rays have been frequently called *Becquerel rays;* this name may be generalised by applying it also to thoric rays, and all rays of that character. I propose, however, the name *radioactive* to describe this phenomenon; *hyperphosphorescence*, which has been proposed, seems to me to give a false idea of its nature.

Polonium.

A certain number of minerals have been examined in a special apparatus designed for the purpose of measuring the conductivity of the air when under the influence of the rays emitted by radioactive substances; among these, pitchblende, chalcolite, autunite, clèveite, monazite, orangite, thorite, &c., were found to be radioactive. All these minerals contained either uranium or thorium, but in some cases the intensity of the action was quite unexpected; thus some pitchblendes were three times as active as metallic uranium; chalcolite (crystallised phosphate of uranium and copper) is twice as active as uranium; autunite (phosphate of uranium and lime) is just as active as uranium. This is in direct contradiction to the results obtained with *pure* uranium compounds which are less active than uranium itself. It therefore seemed probable that the above-mentioned minerals contained a small quantity of a very strongly radioactive body, different to uranium and thorium.

By experimenting it was first noticed that on subliming pitchblende in vacuo an extremely active body was obtained, more than thirty times as active as uranium, but there was very little of it. Eventually, by chemical means, a body was obtained having a radioactivity about 400 times greater than that of uranium. We imagine this to be a new element allied to bismuth, and we propose to call it *polonium.*

The acid solution of pitchblende was treated with sulphuretted hydrogen. The uranium and thorium remain in solution, but the precipitated sulphides are much more active than the original pitchblende. These sulphides contain lead, copper, bismuth, arsenic, and antimony. The active substance contained in the sulphides is insoluble in sulphide of ammonium; this separates it from the arsenic and antimony. The sulphides insoluble in sulphide of ammonium were dissolved in nitric acid; the active substance can be partially separated by sulphuric acid. By exhausting the sulphate of lead with dilute boiling sulphuric acid, a large part of the active substance carried down with the sulphate of lead can be dissolved. This new body which is in solution with the bismuth and copper is completely precipitated by an excess of ammonia; this separates it from the copper. Its separation from bismuth, which now alone remains, is not easy by the wet way; we can, however, obtain an approximate separation by fractional precipitation. For this purpose water is added to the hydrochloric or nitric solution; the portions first precipitated are by far the most active. To obtain a complete separation we must have recourse to sublimation of the sulphides in vacuo at about 700° C. The active sulphides are deposited in the form of a black layer in that portion of the tube which is about 250—300°. The sulphides of bismuth and lead remain in the hotter part of the tube.

The radioactive power of polonium is so great that it seems reasonable to enquire whether uranium and thorium do not owe their activity to the presence of a small quantity of this body. This did not appear probable, for if such was the case different samples of uranium compounds would have very different radioactivities, but in the course of a number of experiments made with various samples of metallic uranium, as well as with oxides and salts from various sources, I have never found any marked difference between the relative activities of the same compound.

Photographic Impressions. Fluorescent Effects Produced by Becquerel Rays.

Uranic, thoric, and polonic rays act on sensitive plates, the rays of thorium being less active than those of uranium.

Uranium compounds give a photographic impression after one hour. The substance we call sulphide of polonium gives a good impression after only three minutes, and there is a decided action noticed after even half a minute.

Uranium and the compounds of thorium have no apparent fluorescent action on platinocyanide of barium,

* At this time (January, 1896), the emission of X-rays, unaccompanied by fluorescence, as in the case of platinum anticathodes, was not yet known.

but sulphide of polonium has a very distinct action. The experiment can be performed in the following manner:—The active substance is spread in a very thin layer over a portion of the surface of a metallic disc, the whole of the disc is covered with a very thin sheet of aluminium of the same diameter. The whole surface of the aluminium is then covered with a thin layer of platinocyanide of barium. On examining this in the dark, a faintly luminous area is noticed on the upper disc, and it is easy to make certain that this area is opposite the active substance. The rays emitted by this latter body have traversed the aluminium and excited the fluorescence of the platinocyanide above it, while the remainder of the disc remains dark. It thus appears that we can obtain an indefinite amount of light without the expenditure of any energy. A similar experiment with the oxides of uranium and thorium was not successful.

Conductivity of Gas under the Influence of Becquerel Rays.

To obtain simple theoretical conditions it is advisable to use plates the surfaces of which are great with regard to their distance apart. By varying the difference of potential between the plates, the strength of the field may be varied. In weak fields the intensity of the current is proportional to the strength of the field; a constant initial conductivity exists. As the field becomes stronger, the current increases less and less quickly, and tends—in the case of very strong fields—towards a practically constant limit.

The intensity of the current increases with the volume of air comprised between the plates; however, as the distance between the plates increases, the fresh layers of air introduced have less and less effect, as if the uranic rays were strongly absorbed by the air they traverse. Not only air, but oxygen, hydrogen, and carbonic acid gas are made conductors by the action of Becquerel rays. The experiments were carried out at the ordinary pressure, but others under variable pressures have also been tried, with the result that for pressures which are not too feeble the current is proportional to the pressure, at least in the cases of air and hydrogen.

The laws of the conductivity of air under the influence of Becquerel rays are analogous to those obtained with X rays. From this point of view we may imagine that gases submitted to the influence of Becquerel rays are partly *ionised*, and that it is the movement of the ions charged with electricity along the lines of the electric field which constitutes the current.

The Absorption of Becquerel's Rays.

To measure the absorption of Becquerel rays by solid bodies, the active substance is covered over with a plate of the material under examination. By this means, the proportion of rays transmitted by a given screen can be determined, provided always that the screen is a sufficiently good conductor. A sheet of aluminium 0·001 m.m. in thickness will only allow a fraction of the rays to pass, equal to 0·2 for uranium and 0·4 for oxide of thorium in a layer 0·005 m.m. thick. If a layer of oxide of thorium 0·006 m.m. thick is used, the same sheet of aluminium will allow rays to pass equal to 0·7.

Experiments published with regard to the reflection and refraction of Becquerel rays are not very conclusive, but the observations made are not comparable with the reflection and refraction of luminous rays.

Analogies and Differences between Becquerel and other Rays.

Becquerel rays are characterised by the following properties:—

They render gases which they traverse conductors of electricity; they produce photographic impressions. These two properties do not in any way depend on the past or present action of light on the bodies emitting these rays. They traverse all substances, glass, paper, metals, and liquids, but are, as a rule, absorbed to a great extent. Their emission appears to be spontaneous; it is constant, and indicates the presence of certain elements in the active substance. Their emission is but slightly influenced by the physical state of the active substance, or by the presence of the small amounts of impurities they may contain. It is important to remember these points when endeavouring to establish analogies and differences between these and other kinds of rays which appear to resemble them.

The spontaneous emission of these rays appears to give rise to a continuous disengagement of energy of which we cannot find the source. This is in direct contradiction with Carnot's principle. While admitting that this giving off of energy exists, it is possible to conceive the production of the phenomenon in different manners. For instance, it may be a phosphorescence of very considerable duration caused by the action of light; but this hypothesis is hardly probable. It may be an emission of matter accompanied by a loss of weight of the radio-active bodies, or the utilisable energy may be constantly diminishing. Again, it may be a secondary emission provoked by rays analogous to X-rays (these being constantly in existence in space, much more penetrating than X-rays, and only commencing to be absorbed by elements of a high atomic weight, such as uranium and thorium). In this last hypothesis we have endeavoured to make the emission of these rays fit in with Carnot's principle, but the question may just as well be asked whether Becquerel rays may not be produced at the expense of the heat in the surrounding medium, contrary to this principle.

Since this research was made, M. and Mdme. Curie have quite recently, in conjunction with G. Bémont, discovered in pitchblende indications of an element (radium) allied to barium in its chemical properties, but differing in its radio-activity, and having a definite line in its spectrum, which is evidence of the existence of a true element (see *Comptes Rendus*, cxxvii., p. 1215; also Chemical News, lxxix., p. 1).—*Revue Générale des Sciences*, Jan. 30, 1899.

THE

SEPARATION OF COPPER AND ANTIMONY.

By M. LUCAS.

One of the most frequently used methods of effecting this separation is to precipitate the two metals in the form of sulphides, and to re-dissolve the sulphide of antimony in sulphide of sodium. Complete separation often requires four or five successive treatments; we can only check the progress of the reaction on very small portions of the liquid, so as not to affect the analysis; and further, there is always a small portion of sulphide of copper dissolved by the sulphide of sodium, and if the antimony is afterwards estimated by electrolysis, this copper will be deposited with it on the cathode.

It seemed to me to be more simple and more advantageous to proceed in the following manner:—After the first treatment with sulphide of sodium, the whole is treated with 5 c.c. of peroxide of hydrogen to destroy the polysulphides, and we then make a preliminary electrolysis following Classen's method, but without previously removing the sulphide of copper which collects at the bottom of the liquid.

The metallic deposit is then weighed, and the liquid heated to re-dissolve the precipitated sulphur, treat with 5 c.c. of peroxide of hydrogen to destroy the polysulphides, add a little sulphide of sodium, and electrolyse again; the second deposit covers the first; weigh these two together and keep the metal.

Do this a third time, but use a different cathode; weigh this third deposit, re-dissolve in nitric acid, and estimate

Composition of the sample.		Amounts of Sb and Cu weighed.							
Pure Sb.	Pure Cu.	First electrolysis. 12 hours.	Second electrolysis. 6 hours.	Third electrolysis. 12 hours.	Fourth electrolysis. 6 hours.	Total Sb.	Cu from cathodes.	Electrolytic Cu.	Total Cu.
0·110	0·096	0·106	0·006	0·0083	0·004 Cu only.	0·110	0·0143	0·0817	0·093
0·0736	0·150	0·0682	0·0043	0·0053	0·0018 Cu only.	0·0739	0·0057	0·1443	0·150
0·100	0·100	0·103	0·0043	0·001 Cu only.	—	0·0995	0·0088	0·0912	0·100
0·107	0·032	0·1075	0·005	0·0025 Cu only.	—	0·1075	0·0075	0·0248	0·0323
0·100	0·100	0·101	0·005	0·004	0·002 Cu only.	0·099	0·013	0·0865	0·0995

the copper colorimetrically to see whether or no there is still a deposition of antimony, and if it is necessary to make a fourth electrolysis.

The deposit of copper and antimony is dissolved in nitric acid and filtered. Treat with ammonia and a few drops of sulphide of ammonium. The sulphide of copper which is precipitated is filtered, re-dissolved, and the copper estimated by colorimetry by means of ferrocyanide of potassium. This amount of copper is deducted from the weight of antimony, and added to that of the copper estimated in the residue. This secondary estimation of the copper is indispensable, no matter in what manner the sulphide of sodium has been used.

Finally, the sulphide of copper is filtered, but only after the major part of the sulphide of sodium has been destroyed by peroxide of hydrogen. I give some figures obtained by this method (see Table).

The fourth analysis was carried out in the presence of 0·098 grm. of pure tin, which was afterwards found by analysis.

This method is a more or less perfect application of the method of separating copper and iron electrically as done by M. Riche, and nickel and iron as done by M. O. Ducru.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 18-19.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 2nd, 1899.

Professor DEWAR, F.R.S., President, in the Chair.

MR. F. W. Dootson was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. James Herbert Allworthy, Laxton School, Oundle; Peter Auchinachie, 12, Mid Street, Keith, N.B.; Kendall Colin Browning, St. John's College, Cambridge; William Collingridge, Port Sanitary Office, Greenwich, S.E; Archibald Glen Kidston Hunter, Dunedin, New Zealand; Lawrence Christopher Panting, 9, Beverley Road, Anerley, S.E.; Samuel Barnett Schryver, D.Sc., Ph.D., 27, Arundel Gardens, W.: Arthur John Shelton, 19, Sturry Street, Poplar, E.; Robert Tatlock Thomson, 156, Bath Street, Glasgow.

Of the following papers those marked * were read:—

*13. "*Maltodextrin, its Oxidation Products and Constitution.* By HORACE T. BROWN, LL.D., F.R.S., and J. H. MILLAR.

The subject of this paper is the maltodextrin which occurs amongst the intermediate products of starch hydrolysis with diastase, and to which the empirical formula—

$$\begin{cases} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_2 \end{cases}$$

has hitherto been assigned (Brown and Morris, *Trans.*, 1885, xlvii., 527). Although present in considerable quantities in starch-transformations which have been arrested at the right point, its preparation in a pure state, and in sufficient amount for extended work, is a very laborious process. When isolated, it was found to have properties corresponding to $[\alpha]_D$ 181—183, and R 42—43, and was completely hydrolysed to maltose by diastase, and to *d* glucose by acids.

When maltodextrin is carefully oxidised with mercuric oxide and barium hydroxide until its power of reducing Fehling's solution disappears, the greater part of the product is obtained as the barium salt of a definite and complex carboxylic acid, which is provisionally called *maltodextrinic acid A*. This has been isolated. Its properties correspond to $[\alpha]_D$ 192·3, R 0, and its calcium salt contains 2·4 per cent of calcium. Maltodextrinic acid A is hydrolysed both by diastase and by dilute acids. Under the action of diastase it yields 40 per cent of maltose, and 60 per cent of another carboxylic acid of less complexity: this is *maltodextrinic acid B*, the calcium salt of which contains 3·8 per cent of calcium.

When hydrolysed by dilute oxalic acid, maltodextrinic acid A yields 85·8 per cent of *d*-glucose, and another still simpler acid which is shown to be a C_5-derivative. Maltodextrinic acid B, when hydrolysed by oxalic acid, also yields this same C_5-acid and 67·7 per cent of glucose.

The final C_5-acid corresponds in composition to $C_5H_{10}O_6$, and appears to be a normal carboxylic acid derived from a pentose. Since this acid can now be prepared in fair quantities by the oxidation of maltose with mercuric oxide, the authors expect to be able very soon to put its exact nature beyond doubt. It has many properties in common with those of xylonic acid.

If the constitutional formula of maltose is taken as—

$$CH_2OH\cdot CHOH\cdot CH\cdot(CHOH)_2\cdot CH\cdot O\cdot CH_2\cdot(CHOH)_4\cdot CHO,$$

the polysaccharide maltodextrin may be regarded as being made up of three such molecules with the elimination of the elements of $2H_2O$. Written in an abbreviated form, the formulæ of maltodextrin and of maltodextrinic acid A may be expressed thus:—

$$O<\begin{matrix} C_{12}H_{21}O_{10} \\ C_{12}H_{20}O_9 \\ C_{12}H_{21}O_{10} \end{matrix}<$$

Maltodextrin.

$$O<\begin{matrix} C_{12}H_{21}O_{10} \\ C_{12}H_{20}O_9 \\ C_5H_9O_5 \end{matrix}$$

Maltodextrinic acid B.

the sign $<$ being used to denote the open carbonyl.

The hydrolysis of maltodextrinic acid A in two successive steps by diastase and acids respectively may be represented in the following manner:—

1. *Diastase Hydrolysis.*

$$O<\begin{matrix} C_{12}H_{21}O_{10} \\ C_{12}H_{20}O_9 \\ C_5H_9O_5 \end{matrix} + H_2O = O<\begin{matrix} C_{12}H_{21}O_{10} \\ C_5H_9O_5 \end{matrix} + C_{12}H_{22}O_{11}$$

Maltodextrinic acid A. Maltodextrinic acid B. Maltose.

2. *Acid Hydrolysis.*

$$O<\begin{matrix}C_{12}H_{21}O_{10}\\C_5H_9O_5\end{matrix} + 2H_2O = C_5H_{10}O_6 + 2C_6H_{12}O_6$$

Malodextrinic acid B. Pentose acid. Glucose.

In an appendix to the paper, the authors describe the standard methods they now employ to determine the amount of glucose which a carbohydrate or its derivative yields on complete hydrolysis with oxalic acid. The results of thus hydrolysing soluble starch, maltose, maltodextrin, and maltobionic acid are given.

*14. "*On Attempts to prepare Pure Starch Derivatives through their Nitrates.*" By HORACE T. BROWN, LL.D., F.R.S., and J. H. MILLAR.

This paper records the efforts made by the authors to obtain some of the hydrolytic products of starch in a pure state by preparing their nitric esters and regenerating them by treatment with ammonium sulphide.

Although perfectly successful as regards soluble starch, it was not found possible to regenerate from their nitrates substances like maltodextrin, amylodextrin, and the stable dextrin, the recovered product always showing signs of having undergone some oxidation during the nitration process. All the reducing starch products, *i.e.*, those with an open carbonyl group, yield on nitration and regeneration indeterminate mixtures containing carboxylic acids.

*15. "*The Stable Dextrin of Starch Transformations, and its relation to Maltodextrin and to Soluble Starch.*" By HORACE T. BROWN, LL.D., F.R.S., and J. H. MILLAR.

When starch is transformed by an active diastase, such as that derived from an air-dried malt, at temperatures below 60°, the reaction proceeds with great rapidity until a resting stage is reached corresponding to $[\alpha]_D$ 150, R 80, for the mixed products of change. At this stage these products consist of maltose, and a dextrin which, comparatively speaking, is very resistant to the further action of the hydrolytic agent. An account is given of the mode of separation, and the dextrin was obtained ultimately with optical and reducing properties corresponding to $[\alpha]_D$ 195—195·7, and R 5·7 to 5·9. This residual reducing power is a property inherent to the dextrin, and is not due to admixture with a second reducing substance. This was shown by oxidising the dextrin with mercuric oxide and baryta, a definite dextrinic acid being produced.

Dextrinic acid is a complex carboxylic acid with distinct but feeble acid properties. It forms a well-defined calcium salt, containing 0·31 per cent of calcium, and under the influence of acid hydrolysis yields *d*-glucose and a residual C_5-acid, which is shown to be identical with that obtained by the complete acid hydrolysis of the two maltodextrinic acids already described. The amount of glucose given by this hydrolysis has been determined.

Dextrinic acid and its salts, and also the dextrin from which it is derived, unlike maltodextrin and maltodextrinic acid A, are but very slowly hydrolysed by diastase. After many hours' treatment at 50—60° a certain limited amount of change takes place, the resulting products being maltose and glucose in about equal proportions. The glucose is not derived from previously formed maltose, since it is observed when a malt-extract absolutely devoid of any maltose-hydrolysing power is employed.

The available evidence all points to the conclusion that the stable dextrin and the derivative polysaccharide acid, dextrinic acid, are built up of C_6-, and not, as in the case of maltodextrin, of C_{12}-groups. The dextrin molecule may be empirically regarded as made up of 39 $C_6H_{10}O_5$ groups in combination with a terminal $C_6H_{12}O_6$ group; or, more correctly, as a condensation of 40 glucose molecules, with the elimination of $39H_2O$. All the known properties of these substances agree with the view that their constitution may be expressed by the formulæ—

$$O_{39}\begin{cases}C_6H_{11}O_5\\(C_6H_{10}O_4)_{38}\\C_6H_{11}O_5\end{cases} \qquad O_{39}\begin{cases}C_6H_{11}O_5\\(C_6H_{10}O_4)_{38}\\C_5H_9O_5\end{cases}$$

Stable dextrin. Dextrinic acid.

The paper concludes with a discussion of the constitution of the starch molecule in the light of this new work.

DISCUSSION.

Dr. ARMSTRONG expressed the opinion that the formulæ suggested by the authors conveyed an idea of instability scarcely in accordance with the behaviour of the compounds in question. He could not help thinking that their structure was such that the ordinarily active groups were in some way shielded from attack or rendered unapproachable. Obviously, however, much more had to be learnt on such subjects. The complexity of the starch molecule was altogether remarkable when it was seen that in plants the formation of starch took place with extraordinary facility, and apparently under very simple conditions: thus starch could be detected in *Spirogyra*, originally depleted of the carbohydrate, after a very few minutes' exposure to light. It was most important to obtain further information on such a matter, as well as on the structure of the starch molecule; he was glad, therefore, that Dr. Brown was also studying the problem from the biological side.

Mr. C. F. CROSS remarked that the production of a C_5-hydroxy-acid under the conditions of the authors' experiments would add another and comparatively simple transition from hexose to pentose derivatives, and further generalise the tendency to form C_5-products—of which lævulinic acid and furfural are typical examples, but contrasted with the present case by complete elimination of alcoholic OH-groups. It would be important to determine whether a C_7-derivative were actually synthesised or the one C-atom in question eliminated as a CO-derivative.

Dr. G. HARRIS MORRIS said that the authors' account of the action of diastase on the stable dextrin probably explained the contradictory statements which had been made by different observers as to the formation of dextrose from maltose under the action of the enzymes of germinated and ungerminated cereals. In working with pure maltose and the cold-water extracts of several cereals, he had been unable to obtain the slightest evidence of any such action except in the case of maize, but others, using malt extracts and starch-conversion products, had obtained indications of the formation of dextrose. It had been assumed that this dextrose was formed by the hydrolysis of the maltose contained in the starch-conversion products, but it would now appear that it resulted from the action of the diastase on the stable dextrin, and that his conclusion that malt obtained no enzyme capable of hydrolysing maltose was correct.

Mr. A. R. LING, in commenting on the observation that the dextrinic acids were well characterised substances, thought it was unfortunate that neither they nor their derivatives were crystalline. This was, perhaps, rather remarkable in the case of the acid of lowest molecular weight. He was glad to hear that the authors had convinced themselves that the so-called stable dextrin was a cupric-reducing substance. Mr. Baker and he had submitted numerous preparations of this dextrin to dialysis and fractional precipitation with aqueous alcohol for several months, and had thus obtained a final product having approximately the same optical and reducing powers as that observed by the authors.

Mr. J. F. BRIGGS asked what was the relation between the stable dextrin of R 5·5 and the dextrin which Dr. Brown formerly obtained by purification by means of mercuric cyanide; the latter had practically no reducing power.

Mr. FENTON said that he was particularly interested in the C_5-acid described by the authors, as, in conjunction with Mr. Jackson, he hoped to prepare a similar acid from erythrose by the hydrogen cyanide reaction.

Dr. BROWN, in reply, stated that the constitution of these reducing polysaccharides can perhaps be explained in the simplest way by regarding them as complexes built up much in the same manner as the hexose residues

of maltose. If the currently accepted explanation of the constitution of maltose ever requires modification, this must of course modify our views as to the exact mode of combination of the constituent groups of the polysaccharides.

The constitution of the C_5-acid is at present occupying the attention of the authors. He agreed with Dr. Morris that these observations will go far to reconcile the conflicting statements with regard to the formation of dextrose from starch by diastase.

The non-reducing dextrins obtained in the older experiments by the mercuric cyanide method were no doubt maltodextrinic and dextrinic acids.

*16. "*Propylbenzenesulphonic Acids.*" By Gerald T. Moody, D.Sc.

The results described in this note have been obtained in the course of an investigation on isomeric change (*Proc.*, 1888, iv., 77; 1892, viii., 90, 213, 214; 1895, xi., 48).

Propylbenzene readily sulphonates when shaken with one and a half times its own volume of ordinary sulphuric acid, and the product consists almost entirely of one propylbenzenesulphonic acid, the amide of which melts at 109—110°. This sulphonamide, on oxidation with potassium permanganate, yields 4-sulphonamidobenzoic acid (m. p. 280°), showing that it is derived from propylbenzene-4-sulphonic acid.

Propylbenzene-3-sulphonic acid and propylbenzene-2-sulphonic acid are obtained by reducing 2-bromopropylbenzene-5(? 3)-sulphonic acid and 4-bromopropylbenzene-2-sulphonic acid respectively. Propylbenzene-3-sulphonamide melts at 57°. Propylbenzene-2 sulphonamide yields 2-sulphonamidobenzoic acid ("saccharin," m. p, 222°) on oxidation with permanganate, and melts at 128°. This melting-point is identical with that of the sulphonamide of the second acid obtained in small quantity on direct sulphonation, and is much higher than either that recorded by R. Meyer, or that by Claus for the sulphonamide obtained by them respectively from the acid which they consider to be propylbenzene-2-sulphonic acid, and regard as one of the products of direct sulphonation. It is to be noted, however, that these authors do not appear to have taken the precaution of purifying the hydrocarbon employed by them, and it is extremely likely that the fuming acid used gave rise to disulphonic acid.

Propylbenzene-3-sulphonic acid and propylbenzene-2-sulphonic acid do not undergo isomeric change when heated for several hours at 150°. The stability of the latter acid, compared with that of ethylbenzene-2-sulphonic acid, which is converted into ethylbenzene-4-sulphonic acid at the temperature of the water-bath, is remarkable, more particularly when considered in conjunction with the fact that propylbenzene-2-sulphonic acid is either not formed, or, if formed direct, is produced only in small quantity by the direct sulphonation of propylbenzene.

The author proposes next to investigate the products of sulphonation of isopropyl benzene, more particularly with reference to Claus's statement that the primary product is the parasulphonic acid, and that this is converted into ortho-derivative both on heating at the temperature of the water-bath and on allowing it to remain for ten weeks in sulphuric acid solution.

(To be continued).

PHYSICAL SOCIETY.

Annual General Meeting, February 10th, 1899.

Mr. Shelford Bidwell, F.R.S., President, in the Chair.

The Report of the Council was read by Mr. H. M. Elder.

Dr. Atkinson then presented the Treasurer's Report, and showed that, although there was only a small balance in the bank, the financial position had somewhat improved. The list of Fellows lost to the Society by death was read: the obituary includes the names of Latimer Clark, C.E., F.R.S. Sir James Douglass, F.R.S.; John Hopkinson, D.Sc., F.R.S.; J. E. Myers; Eugene Obach; Henry Perigal, F.R.A.S.; and Bartholomew Price, M.A., F.R.S.

After some remarks with regard to the library and the subscriptions, votes of thanks were passed to the Council, the Auditors, and to the other Officers of the Society.

The President then moved a vote of thanks to the Chemical Society for the use of the rooms at Burlington House.

Council and Officers for the forthcoming year were elected as follows:—

President—Oliver J. Lodge, D.Sc., F.R.S.

Vice-Presidents, who have filled the Office of President—Dr. J. H. Gladstone, F.R.S.; Prof. G. C. Foster, F.R.S.; Prof. W. G. Adams, M.A., F.R.S.; The Lord Kelvin, D.C.L., LL.D., F.R.S.; Prof. R. B. Clifton, M.A., F.R.S.; Prof. A. W. Reinold, M.A., F.R.S.; Prof. W. E. Ayrton, F.R.S.; Prof. G. F. Fitzgerald, M.A., F.R.S.; Prof. A. W. Rücker, M.A., F.R.S.; Capt. W. de W. Abney, R.E., C.B., D.C.L., F.R.S.; Shelford Bidwell, M.A., LL.B., F.R.S.

Vice-Presidents—T. H. Blakesley, M.A.; C. Vernon Boys, F.R.S.; G. Griffith, M.A.; Prof. J. Perry, D.Sc., F.R.S.

Secretaries—W. Watson, B.Sc. (Physical Laboratory, South Kensington); and H. M. Elder, M.A. (50, City Road, E.C.).

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—Dr. E. Atkinson.

Librarian—W. Watson, B.Sc.

Other Members of Council—Prof. H. E. Armstrong, D.Sc., F.R.S.; Walter Baily, M.A.; R. E. Crompton; Prof. J. D. Everett, D.C.L., F.R.S.; Prof. A. Gray, LL.D., F.R.S.; E. H. Griffiths, M.A., F.R.S.; Prof. J. Viriamu Jones, M.A., F.R.S.; S. Lupton, M.A.; Prof. G. M. Minchin, M.A., F.R.S.; and J. Walker, M.A.

The newly-elected President, Prof. Oliver Lodge, then took the Chair, and an Ordinary Meeting was held. In his Address he referred to the heavy death-roll of the Society during the past year, and to the tribute paid to the memory of John Hopkinson at Cambridge University. Prof. Lodge then commented on the quickness with which scientific discoveries were now applied to practice, and to the interest taken in such applications by men of science. He did not know whether this was due to the example and inspiration of Lord Kelvin, or to the progress of education among the public. He regretted that the public was so ignorant of scientific subjects. Rapidly reviewing the work done in Physics during the past year, he spoke of the experiments of Righi, Preston, Michelson, and J. J. Thomson, and called attention to a prediction lately published in *Nature*, by Prof. G. F. Fitzgerald, with regard to the probability of being able to obtain magnetic effects by passing circularly polarised light through absorptive media. After commenting upon the important position now occupied by Terrestrial Magnetism among the Sciences, and to the advantages of the publication now known as *Science Abstracts*, Prof. Lodge said there was one event of exceptional significance to Physics that had happened during the past year, an event of which Science would feel the effect for centuries to come—the Government had decided to begin to establish a National Laboratory. He wished to congratulate Sir Douglas Galton, and himself, on the speedy result of their urging the matter upon the British Association. He thought the thanks of the Physical Society were due to the Committee appointed by the Treasury, especially perhaps to Prof. Rücker, as Acting-Chairman of that Committee, and to Mr. Chalmers, who represented the Treasury, for

the way in which the work had been brought to an issue. There was much for which the present Government deserved praise during the past year; he wished there could be added to their laurels the inauguration of a University for London. Prof. Lodge then went on to the specific subject of his Address—the opacity of conducting media to light and to electric waves generally, emphasizing the brilliant work of Mr. Oliver Heaviside in unifying phenomena apparently different, discussing the effect of boundaries, and dealing specially with the question—first attacked by Maxwell—of the theoretical opacity of gold-leaf. This part of the Address will be published in full in the *Phil. Magazine*.

Prof. Ayrton said, with regard to the attenuation of electric waves by the earth, that Mr. Whitehead, some months ago, came to the conclusion that when the primary and secondary coils were placed flat on the earth, at a distance from one another, nearly all the energy of the primary was absorbed by the earth before reaching the secondary. The degree of absorption was so great that Mr. Whitehead had hesitated to publish his theoretical results until experiment should confirm them.

Prof. Lodge concurred with Mr. Whitehead's result. Three cases were to be considered. In the first, one horizontal coil is superposed to the other, with sea-water or some other absorbing medium between them; in this case the absorption at moderate distances is not excessive. But of course if the coils are formed of cable sheathed with iron, as in the recent experiments made by the Royal Commission, the iron itself prevents the progress of electric waves from primary to secondary. In the second case the coils are wholly in the same horizontal plane: the earth, owing to its great magnitude, behaves almost as a perfect conductor; if the coils are now near the earth, there is no normal magnetic force between them—it is all tangential. In the third case the coils are opposed to one another, both being vertical and near to the earth. The high conductivity of the earth is here acting to the advantage of wave propagation, for the image of the primary coil is in phase with the coil itself, and the total effect is approximately doubled.

Prof. Carey Foster then took the Chair, and Prof. Oliver Lodge read a paper by Mr. Benjamin Davies on "*A New Form of Ampere-meter and Voltmeter with a Long Scale.*" These instruments are already well known, although no account of them has actually been published. They are of the moving-coil, long-range, portable type, with a very uniform scale from zero to maximum. The magnetic circuit has only one air-gap, which is generally the space between a central cylinder of iron or steel and a concentric tube of iron, modified in various ways for facilitating the adjustment of the magnetic induction and the placing of the coil. The central cylinder is bored axially, and one side of the rectangular coil is pivoted at the top and bottom of the hole thus made. The second side of the coil moves in a circular path in the annular air-gap. Photographs of the instruments in several modified forms were exhibited.

Prof. Ayrton said the instruments appeared to be very successful; he could bear witness of their value particularly as regards the length of range. The general principle by which long range was to be obtained on moving-coil, portable instruments, was developed some ten years ago by M. Carpentier, of Paris, who used a central magnet surrounded by a concentric hollow cylinder, with only one side of the coil in the magnetic gap between them; but it was not then a portable form of instrument, for the coil was suspended. Prof. Ayrton had himself worked in this direction in the "static station volt-meter." In that instrument there were three magnetic circuits arranged to give staticism; this was described in 1892 or 1893.

The Vice-President (Prof. Carey Foster) proposed a vote of thanks to the author, and the meeting adjourned until February 24th.

NOTICES OF BOOKS.

Electrolysis and Electrosynthesis of Organic Compounds. By Walther Loeb. Authorised Translation from the Author's Enlarged and Revised Edition, by H. W. F. Lorenz. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1898. Pp. xiii.—103. 12mo.

The electrolysis of inorganic compounds has obtained a recognised position in pure and applied science, but the great difficulties attending attempts to carry out the synthesis or decomposition of organic compounds has prevented securing entirely satisfactory results. In inorganic electrolysis the development has been regular and systematic, but organic compounds yield such diverse and complex results that the history of this branch of electrolysis is largely a collection of incoherent facts. Feeling this, Dr. Loeb undertook to compile, from the literature scattered through numberless periodicals, a summary of the investigations of the many workers in this fertile field. Such was the origin of the little book which now appears in an English dress. The investigations summarised are arranged in systematic order—hydroxyl compounds, ketones, acids, &c. Due credit is given to the several chemists for their part in each case, and in nearly all cases references to literature are given, so that the footnotes constitute a bibliography of the subject.

Some of the processes have become of industrial value, the preparation of iodoform by the electrolysis of ethyl alcohol in alkaline iodide solution is an example; and patents have been taken out for the preparation of valuable substances in the aromatic series.

The book is a very useful summary; the translator has done his work well. The abbreviation "Chem. Ber." for "Ber. d. Chem. Ges." looks unfamiliar. A key to abbreviations might be added in a second edition. The chief blemish to this work is the absence of dates in connection with references to periodical literature.

H. C. B.

An Experimental Course of Chemistry for Agricultural Students. By T. S. Dymond, F.I.C., Lecturer on Chemistry and Agricultural Chemistry in the County Technical Laboratories, Chelmsford. London: Edward Arnold, 37, Bedford Street, Strand.

This work, under the general editorship of Professor R. Meldola, F.R.S., is intended to meet the needs of agricultural students in the rural districts, the special aim being to give the intending farmer training in accuracy, careful observation, and a knowledge of the elementary principles of chemical change and of the properties of certain chemical substances, both organic and inorganic.

As the customary four years' course of organic and inorganic chemistry goes far beyond the requirements of an agricultural student, the present course has been restricted as far as possible to the study of the chemical substances with which agriculture is concerned.

There are plenty of illustrations, and the problems set for the student are clear and to the point, and, if conscientiously worked out, cannot fail to be of great value.

Practical Inorganic Chemistry for Advanced Students. By Chapman Jones, F.I.C. London: Macmillan and Co. 1898. Pp. 239.

We object to part of the title the author has chosen for his book: instead of "advanced students" he should have said "beginners." He tells us that this text-book is specially intended for the use of students working according to the arrangements made by the Department of Science and Art, but the bulk of the information herein

given should be acquired by first year's students, or "beginners." We cannot imagine an advanced student requiring a description accompanied by an illustration, as on page 48, of how to make a loop at the end of a platinum wire.

The book is divided into three parts. Part I. on preparations, and exercises in manipulation, including the preparation of gases by the use of hot and cold liquids and dry substances, distillation, &c. Part II. introduces qualitative analysis, and deals *seriatim* with the five groups and their sections; and in Part III. we have quantitative volumetric analysis, and the preparation of standard solutions.

The Smithsonian Institution, 1846—1896. The History of its First Half-century. Edited by George Brown Goode. City of Washington. 1897. Pp. 856.

The Smithsonian Institute was established in 1846, by a law signed by President Polk on the 10th August of that year, and the first meeting of the Board of Regents was held on the 7th September following. The splendid volume now before us gives the history of this Institution from that time to the end of its first fifty years of existence.

The plan of the volume was drawn up by Dr. G. Brown Goode, and, on its approval, the editing was undertaken by the late Dr. James C. Welling. The unfortunate death of this gentleman, however, greatly delayed the work, until it was undertaken and carried to a successful issue by Dr. Goode.

The book begins with a short Preface by the President of the United States, the remainder being divided into two great Sections. Section I., of fifteen chapters, is entitled "History of the Smithsonian Institution," and Section II., also of fifteen chapters, is called "Appreciations of the Work of the Smithsonian Institution."

In Section I. we first find a biography of James Smithson, who was, through his mother, lineally descended from Henry VII. of England: this is followed by chapters on the founding of the Institution, the establishment of the Board of Regents, the Secretaries, the Benefactors, the Buildings, Grounds, Library, Museums, &c. The publications and exploration works of the Institute are also dealt with by competent writers, and the Section closes with a biographical sketch of Dr. G. Brown Goode, by David S. Jordan.

Section II. consists of a series of essays and monographs on the various scientific subjects which have engaged the attention of the Smithsonian Institution; thus we have Physics by Prof. Mendenhall, Astronomy by Edward S. Holden of the Lick Observatory, Palæontology by Prof. Cope, Zoology by Prof. Gill, and Bibliography by Prof. H. Carrington Bolton, &c.

The book is adorned with a number of excellent portraits; it is well printed in clear bold type, and will be an ornament to any library.

Calculations concerning Water-pipes. ("Kálkulos sobre las Kañerias de Agua"). By A. E. Salazar, Professor of Physics at the University of Chile. With the Original Diagrams and Tables. Santiago de Chile: Hume I Ka, Armada. 1898. Pp. 246.

This is essentially a mathematical work for water engineers, and deals entirely with calculations for determining the size, shape, and positions of water pipes and aqueducts, with regard to the flow of water through them, with respect to both rate and power, loss by friction, &c., and with hydraulics and turbines.

The book is divided into eight chapters and an Appendix, there are seventeen figures and ten tables, as well as a good Index. The book is printed on good paper, and, unlike most foreign works, is well bound in a stiff cover.

CORRESPONDENCE.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

To the Editor of the Chemical News.

Sir,—I have to thank Mr. F. W. Daw for his opinion as to the cause of the low results when a permanganate solution standardised with iron is used to titrate manganous salts.

He says "that the usually accepted equation for the action of permanganate on manganous sulphate does not, *in the circumstances under discussion*, quite represent the reaction taking place." This statement does not convey the information it was intended to, because I do not know whether the phrase italicised refers to the circumstances under which I worked when the low results were attributed to traces of carbon in the iron, or to the circumstances he describes in his recent article (Chem. News, lxxix., 25). The importance of this distinction lies in the fear that the separate processes would give different results when the same sample was operated upon. The fact is that the precipitated oxides of manganese approximate variously to MnO_2 with varying modes of procedure, and from the work of Wright and Menke (*Journ. Chem. Soc.*, 1880, p. 36) it might be inferred that the oxides precipitated by Mr. Daw's procedure are deficient in oxygen.

I was not unaware of the work of Gooch and Austen, to which my attention is next called. It is only fair, however, to say that under what they consider the best circumstances their opinion of the method is little short of the "faint praise which damns." For instance, it is certainly unfortunate that the experimentalists on whom whom Mr. Daw leans should say "The inference is plain that the estimation of manganese in the form of mangonoso-manganic oxide, Mn_3O_4, is by no means to be considered utterly untrustworthy when the process is conducted in the manner described, though it must be recognised that an irregular result may occur occasionally." This is hardly a satisfactory recommendation for a standardisation process at all, much less for a process by the results of which the validity of this or that means of standardising shall be measured.

So as not to be misunderstood, I must remark that it is not the weighing as Mn_3O_4 which I have questioned, but only the final heating of it, in platinum crucibles, over a naked Bunsen flame. That this practice is fraught with danger is shown by the experience of Wright and Luff (*Journ. Chem. Soc.*, 1878, p. 520), who obtained a manganoso-manganic compound, containing too much oxygen, and by Pickering (Chem. News, xliii., 226) who found the percentage of manganese vary from 69·688 to 74·997. These results have been used to good purpose by those chemists who favoured the precipitation of manganese as the ammonium phosphate and the weighing as pyrophosphate.

Morse and Burton (*Am. Chem. Journ.*, x., 2, and Chem. News, lvii., 176) showed that the constant loss of weight when zinc oxide is heated in platinum vessels over a gas flame is due to the permeability of that metal to reducing gases, an explanation which Pickering had previously suggested to account for his variant manganese results. Since that time I believe that generally direct contact of flame has been avoided. This much is certain, that Wright and Luff found strong ignition, *after surrounding the capsule with a clay jacketing*, to yield a compound closely approximating to Mn_3O_4; that Fresenius ("Quant. Anal.," p. 202, 7th ed.), says the oxides, *ignited out of contact with reducing gases*, gives Mn_3O_4; and that nearly every writer who recommends this method of estimating manganese especially mentions strong ignition *in a muffle furnace*.

I beg, finally, to say that I have never been seriously engaged, experimentally, with the points under discussion;

I therefore write by no means dogmatically. At the same time I have been so far interested as to read whatever papers of a relevant nature were available, and the almost unanimous opinion seems to be that, although it is not *impossible* to produce Mn_3O_4 in the way Mr. Daw describes, it certainly is not a good method to employ.—I am, &c.,

HARRY BREARLEY.

Totley, near Sheffield.

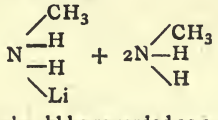
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 1, January 2, 1899.

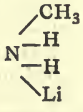
General Method of Separating Mixtures of Chloride, Bromide, and Iodide of Silver.—H. Baubigny.—The author refers to the beginning of this research which he has already published, and he now states that he has confirmed his former method of separating chloride, bromide, and iodide of silver quantitatively. The method of employing oxidising agents is a practical and rapid method of recognising the presence of bromine in a mixture of silver halogen salts. The precipitate, whilst still wet, is treated with nitric acid and crystals of permanganate. This mixture transforms the iodide into iodate, and does not sensibly act on silver chloride, whilst the bromide is attacked very slowly. As fluorescin paper is exceedingly sensitive to bromine vapour, mere traces can be detected with certainty.

Preparation and Properties of Lithium-Monomethylammonium.—Henri Moissan.—This paper deals with the extension to compound ammonias of the reaction by which lithium-ammonium and calcium-ammonium were obtained. The cases of liquefied methylamine in contact with the metals potassium, sodium, lithium, and calcium were investigated. At temperatures between $+20°$ and $-50°$ potassium, sodium, and calcium gave no immediate or subsequent combination. Lithium, on the contrary, gave a blue solution, with evolution of heat; towards $0°$ the composition of this product approximates to the formula—

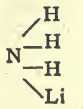


$$+ \; 2N(CH_3)H_2 \quad \text{or} \quad (NH_2CH_3)_3Li,$$

and should be regarded as a solution of the lithium-methylammonium in methylamine. On allowing the compound to dissociate, either in vacuo at the ordinary temperature, or by warming, till a small quantity of the metal appears permanently, a blue solid body is easily obtained, corresponding to the formula—



which is an organic ammonium analogous to lithium-ammonium—



It is stable at ordinary temperatures; reacts with violence on carbon tetrachloride, chloroform, and ethyl iodide; fixes oxygen and nitrogen in the cold, but has no action on hydrogen.

MEETINGS FOR THE WEEK.

MONDAY, 20th.—Society of Arts, 8 (Cantor Lectures). "Cycle Construction and Design," by Archibald Sharpe, A.M.Inst.C.E.

TUESDAY, 21st.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

—— Society of Arts, 8. "Vitreous Enamels," by Cyril Davenport.

WEDNESDAY, 22nd.—Society of Arts, 8. "Electric Traction and its Application to Railway Work," by Philip Dawson.

THURSDAY, 23rd.—Royal Institution, 3. "Toxins and Antitoxins," by Dr. Allan Macfadyen, M.R.C.S.

FRIDAY, 24th.—Royal Institution, 9. "Coherers," by Prof. Oliver Lodge, F.R.S., &c.

—— Physical, 5. "The Joule-Thomson Thermal Effect," by E. F. J. Love, M.A. "A Study of an Apparatus for the Determination of the Rate of Diffusion of Solids dissolved in Liquids" and "Note on the Source of Energy in Diffusive Convection," by Albert Griffiths, M.Sc.

SATURDAY, 25th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

TO CORRESPONDENTS.

C. B. H. D.—A complete list of elements, with their atomic weights, will be found in our last volume (CHEM. NEWS, vol. lxxviii., p. 194).

The BIRMINGHAM TAME AND REA DISTRICT DRAINAGE BOARD require the services of a properly qualified ANALYTICAL CHEMIST to act under the general direction of the Engineer in connection with the Board's Sewage Purification Works.

He must have had practical experience in the Quantitative and Qualitative Analysis of Water and Sewage. Experience in Bacteriological Investigations will be considered an additional qualification.

Commencing Salary, £135 per annum, rising to £165 per annum.

The appointment to be subject to One Month's Notice on either side.

Applications, stating age and qualifications, and endorsed "Analyst," together with not more than three recent testimonials, to be sent to me not later than March 6th, 1899.

(By Order) J. KNIGHT,
Engineer to the Board.

Offices of the Drainage Board,
Council House, Birmingham,
February 14th, 1899.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2048.

MODIFIED FORMS OF APPARATUS FOR THE ESTIMATION OF HALOGENS AND OF AMMONIA.

By F. D. CHATTAWAY, M.A., and K. J. P. ORTON, M.A.

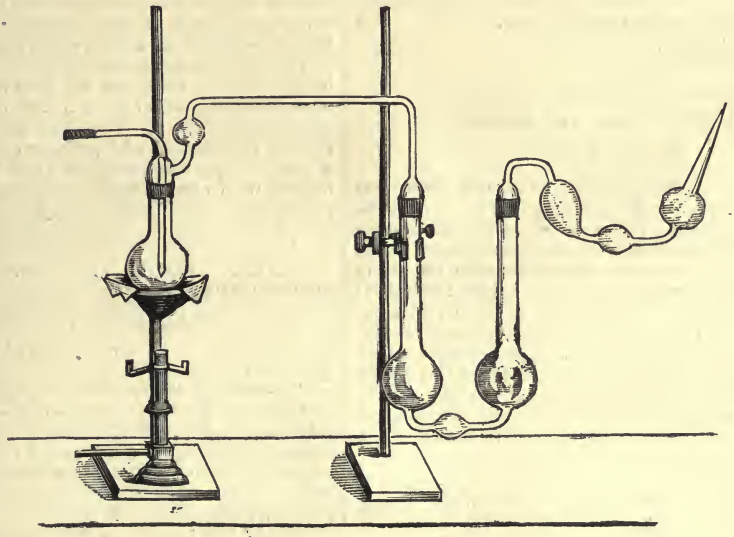
THE apparatus ordinarily figured in text-books for use in the volumetric estimation of a halogen or of ammonia is not very convenient. We have recently had occasion to make a large number of such analyses, and have employed modifications which may prove of service to other chemists.

Apparatus for Estimation of Halogens by Distilling them into a Solution of Potassium Iodide.

This (Fig. 1) consists of a flask of about 300 c.c. capacity, closed by a hollow ground-glass stopper into which are sealed two tubes, one of narrow bore leading to the bottom of the flask, and the other of wider bore, blown into a bulb above the stopper, connecting the flask with a U-tube which is attached by its other limb to an absorption apparatus.

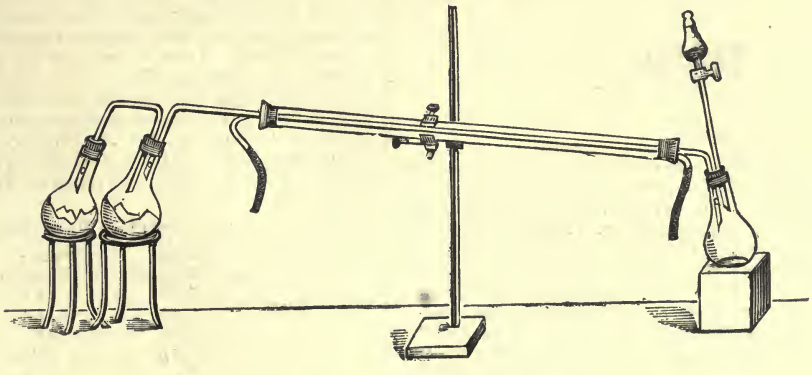
The parts are all carefully ground together, so that the evolved halogen can never come into contact with any oxidisable material—an absolutely essential point if great accuracy be needed. The distillation is conducted in a slow stream of carbon dioxide, led to the bottom of the flask by the fine tube. This ensures regular boiling, so that the distillation requires little attention, and prevents any oxidation of the hydriodic acid, which, when acid solutions are distilled, is always liberated from the potassium iodide used to retain the product. As a further protection it is advisable to add a little finely-powdered calcium carbonate to the potassium iodide solution.

The U-tube is cooled in a beaker of water, and it is well to wrap a piece of filter-paper round the limb heated by the steam, keeping it moist by allowing it to dip below the surface. The apparatus is somewhat cheaper and very little less efficient if the final absorption bulbs, which are used to prevent any possible loss of iodine, are connected with the U-tube by an indiarubber stopper, but the distillation cannot then be carried out so quickly.



$\frac{1}{10}$TH ACTUAL SIZE

FIG. 1.



$\frac{1}{12}$TH ACTUAL SIZE

FIG. 2.

Apparatus for Estimation of Ammonia or of Nitrates and Nitrites by Reduction.

This (Fig. 2) is a modification of Harcourt's apparatus (*Journ. Chem. Soc.*, xv., 385).

The ends of the bent inner tube of the condenser and of the tube connecting the distilling flasks are cut or ground off at a sharp angle, and in each, except the delivery tube into the second flask, a small hole is blown about 2 c.m. below the stopper.

The inner condenser-tube is bent at its lower end, so as to pass vertically into a 300 c.c. flask which serves as a receiver. Through the stopper of this flask also passes the stem of a tap funnel which is half filled with glass beads. Standard acid is added to the receiver through the tap funnel, which serves as a very efficient scrubber.

The second flask should be boiling quietly before the first flask containing the alkaline liquid is heated; twenty to thirty minutes' boiling is sufficient to complete an ammonia distillation. On detaching the flask and rinsing out into it the tap funnel and the end of the condenser tube through the small hole, the contents are ready for titration.

The distilling flasks in this and the preceding apparatus are conveniently heated in cups made of thin asbestos board, or thicker board split; this is soaked with water, moulded to the shape of the flask, then dried and detached. Such cups prevent bumping in most cases.

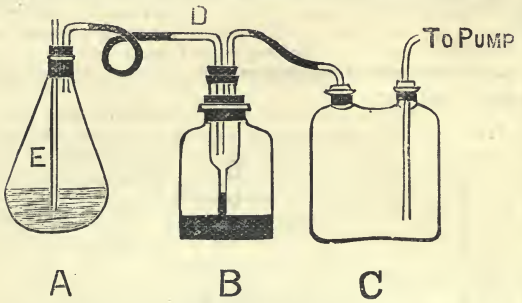
Chemical Laboratory,
St. Bartholomew's Hospital, E.C.

A FILTER-PUMP ACCESSORY.

By HORACE JERVIS.

THREE years ago (CHEM. NEWS, lxxiv., 63) there was described an arrangement for agitating liquids by drawing a current of air through a series of properly fitted and arranged flasks by means of an ordinary filter-tube or pump. The apparatus is described in connection with its use in dissolving steel in copper ammonium chloride solution; it is in this same capacity I have had experience with it.

Until a few months ago a particular filter-tube was supplied with water from a cistern. For certain reasons the supply had to be drawn directly from the main, which, as we were placed higher than any other users on the same service, caused the supply to be very irregular in amount when the cock remained a fixed distance open.



On several occasions since the alteration was made it has happened that the suction has ceased, and a back pressure has pushed the copper solution nearly, if not altogether, into the adjacent flasks. This appears to be caused by a sudden rush of water having no easier means of escape than *up* the tube into the reservoir bottle C (see figure). I have known a similar effect to be due to the stopping up of one of the inlet tubes, whereby the vacuum became great enough to draw the water the wrong way.

From the former cause the occurrence has become frequent enough to warrant special precautions being taken to prevent it. Where the agitated liquid would leave no trace, did such a thing happen, some precaution seems advisable, even if the danger appears remote.

The figure represents the reservoir bottle, C, the dissolving flask, A, and the safety arrangement, B, when the operation is proceeding as usual. The latter piece of apparatus is one of several forms which have been tried. It is particularly chosen for illustration because it can be made to serve a double purpose.

A verbal description is hardly necessary. The drawn out tube is held firmly, but not air-tight, in the neck of the bottle; its tip dips just below the surface of the mercury. No air can be drawn through this arrangement, because the tube is so narrowed that a considerable pressure can be indicated without sensibly lowering the general level of mercury; but if from any cause the water runs back into C, the compressed air finds escape by pushing the mercury below the bottom of the drawn out tube before the solution in the dissolving flask is pushed beyond any desired point on the straight tube, E. (This statement becomes less and less true as the number of flasks are increased). There is thus no possibility of copper solution passing from one flask to the other.

By pouring mercury into the bottle until it nearly reaches the lower end of the larger tube D, which passes through the doubly perforated stopper, the apparatus becomes also an arrangement whereby the degree of exhaustion is kept constant. As soon as the pump is started, mercury rises so far that the end of the tube D is covered; after that varying suction is exactly counterbalanced by the varying height to which the mercury will rise.

The first of these purposes is most simply accomplished by allowing a drawn out leg of a three-way tube, whose other ends are attached to A and C, to pass into a bottle containing mercury. The latter purpose, I am reminded, is more elaborately, and perhaps better, accomplished by a piece of apparatus used by Theo. W. Richards in connection with vapour density determinations under reduced pressure (CHEM. NEWS, lix., 39).

THE PRODUCTION OF CHLORATES BY ELECTROLYSIS FROM SOLUTIONS OF CHLORIDE OF CALCIUM.

By F. ŒTTEL.

THE results I have obtained by the electrolysis of solutions of chloride of calcium confirm the indications recently furnished by Bischoff and Fœrster. The very slight importance of the losses by reduction is attributed to the formation of a thin layer of hydrate of calcium on the cathode; this layer acts as a diaphragm. The electro-chemical activity of this slight skin does not, however, appear to depend upon its being thick; since, on the one hand, excellent results have been obtained with an extremely thin membrane; and, on the other hand, a diaphragm of 2 m.m. in thickness was practically without effect. The production—and what is of more importance, the preservation—of a good membrane requires great care and experience.

The following table shows the normal course of an electrolysis. The solution of chloride of calcium contained 130—150 grms. of the salt per litre, and a little milk of lime was added to precipitate the magnesia. The density of the current was 900 ampères per square metre of anode and cathode; the difference of potential varied between 3·8 and 4 volts, and the temperature was kept up to 75° C.

Duration from the commencement. Hours.	Useful return from the current. Per cent.	Decomposition of water. Per cent.	Reduction. Per cent.
¼	71·8	4·1	24·1
½	76·3	11·4	12·3
1	78·2	12·5	9·3
3	79·7	16·5	3·8
5	83·1	12·9	4·0
8	81·1	12·5	6·4
10	81·9	11·4	6 7
22	83·3	12·5	4·2

It should be noted that the useful return from the current increases during the first few hours, and then remains practically constant at about 80 per cent.

The distribution of the remaining 20 per cent between the decomposition of water and the reduction of the already-formed hypochlorite is very variable.

In another experiment I obtained:—

Useful return from the current ..	79	per cent
Decomposition of water..	9	,,
Reduction	12	,,
	100	,,

These results were considered to be very satisfactory, and I have endeavoured to utilise them for the following purposes:—

1. To electrolyse chloride of calcium to form chlorate.
2. By adding chloride of potassium to precipitate chlorate of potassium, and thus re-generate the chloride of lime to be electrolysed over again.

By following this plan I obtained some altogether unexpected results. The presence of chloride of potassium in the solution caused the formation of thick crusts on the cathode. These crusts were gradually destroyed, and at the same time free chlorine (not hypochlorous acid) was given off simultaneously with hydrogen. I was led to the conclusion that the character of the deposit formed on the cathode is such that it cannot re-dissolve with sufficient rapidity to fix the chlorine. Further, the properties of this deposit are very variable. In one experiment a thin layer was sufficient to stop the disengagement of chlorine; in another trial, the layer disappeared completely, to give place to the thick crusts I have just spoken about, while at the same time chlorine was evolved.

By cooling the electrolyte, I could often obtain crystals of oxychloride of calcium in long needles; and I have every reason to believe that this substance plays an important part in the electrolysis.

It is possible that the curious phenomenon I observed on the addition of chloride of potassium to the solution may be connected with, not the formation, but the solubility of the oxychloride in the chloride of potassium, and that the crusts which are formed on the cathode are not the hydrate, but an insoluble oxychloride of calcium.

The electrolysis of solutions of chloride of calcium is further subject to other disturbing influences. In one experiment I performed, a quantity of chloride of copper which had formed on the surface of one of the conductors became detached from the wire and fell into the electrolytic bath, where it was transformed into oxide. This oxide, acting in its turn on the hypochlorite, decomposed it, at the same time setting free a quantity of oxygen. Other analogous substances, such as the oxides of iron, nickel, and lead, act in a similar manner, so that all sorts of precautions must be constantly taken if we wish to judge the results of an experiment from a single analysis of the gas.

This point appears to be well established by the following figures, obtained by the electrolysis of chloride of calcium in the presence of oxide of copper.

	Useful return from the current. Per cent.	Decomposition of water. Per cent.	Reduction. Per cent.
Apparent	30·9	57·2	11·9
Real	73·3	14·7	12·0

The second—or true—figures were obtained by calculations based on the measurement of the oxygen given off by the action of the oxide of copper during the same time (three minutes)—the circuit being open. From the results I have obtained I am brought to the conclusion that the electrolytic production of chlorates is accomplished by two distinct actions, which may, however, be sometimes combined:—

a. The production of the chlorate by the intermediary of the hypochlorite. The first products formed (alkali and chlorine) combine to form the hypochlorite. This hypochlorite, under the further action of the chlorine, and also by simultaneous direct oxidation, is transformed into chlorate.

b. The production of chlorate by the direct union of the chlorine and oxygen simultaneously set free at the anode.

In a neutral solution it is the *a* reaction that predominates. In a strongly alkaline solution, the other (*b*) reaction occurs. Finally, in a slightly alkaline solution, the two reactions take place simultaneously; it being always understood that the density of the current is the same in each case.

In the electrolysis of chloride of calcium in particular, the *a* reaction is the predominating one. Similar solutions show a tendency to become slightly acid on account of the formation of free hypochlorous acid. In the case of alkaline chlorides, the position of the electrodes and the density of the current are the principal causes which influence both the liberation of chlorine and the formation of a slight excess of free alkali.—*Zeitschrift für Electrochemie*, v., [1], 1—5.

THE ESTIMATION OF PHOSPHORIC ACID IN SUPERPHOSPHATES.

By LEO VIGNON.

As is well known, the estimation of soluble phosphoric acid in superphosphates and in chemical manures comprises practically three cases:—

1. Estimation of the phosphoric acid soluble in water.
2. Estimation of the phosphoric acid soluble in water and the phosphoric acid soluble in citrate of ammonia *together*.
3. Separate estimations of the phosphoric acid soluble in water and that soluble in citrate of ammonia.

The experiments described in this paper have to do only with the last case.

For the separate estimation of the phosphoric acid soluble in water and that soluble in citrate of ammonia it is usual to proceed in the following manner:—

The phosphate is first exhausted with water, then the residue is collected and treated with citrate of ammonia. We then precipitate *separately* the phosphoric acid in both the aqueous and citrate solutions in the state of ammoniomagnesic phosphate. All these operations must be carried out strictly according to the rules laid down by the Committee of Agronomic Stations and Agricultural Laboratories.

I have observed that if the sample contains much phosphoric acid soluble in water and only a small quantity soluble in citrate of ammonia, the precipitation of the latter form of phosphoric acid is not always complete, even after standing for several hours.

Samples of superphosphates treated in the way I have just described have given the following results:—

1. *After Eight Hours.*

	Bone superphosphates.	Mineral superphosphates.	
	I.	II.	III.
Phosphoric acid soluble in water	14·32	14·13	10·20
,, ,, ,, citrate	0·77	0·27	3·10
Total	15·09	14·40	13·30

2. *After Fifteen Hours.*

Phosphoric acid soluble in water	14·32	14·13	10·20
,, ,, ,, citrate	1·08	0·45	3·18
Total	15·40	14·58	13·38

The results are again different if we first mix the aqueous solution with the solution obtained by exhausting

with citrate of ammonia. In fact, for the superphosphate examined I obtained after standing for twelve hours :—

	Bone superphosphates.	Mineral superphosphates.	
	I.	II.	III.
Phosphoric acid soluble in water and in citrate (mixed)	17·79	13·94	14·91
From which we deduce—			
Phosphoric Acid Soluble in Citrate.			
By direct estimation	1·08	0·45	3·18
By difference	3·47	0·81	3·71

We are thus liable, by direct estimation, to find too low figures for the phosphoric acid soluble in the citrate when it is only present in small quantities. It is true that the formation of the ammonio-magnesic phosphate may be helped by continuous mechanical agitation, and by raising the temperature to 25—30°; but these conditions complicate the analysis, and besides may not always be convenient to apply. The method of estimation by difference is more to be trusted.

It is easy to understand why the ammonio-magnesic phosphate, by reason of its mass, has a greater tendency to come down integrally in a shorter time in the aqueous and citrate mixture than in the citrate alone, which might be very poor in phosphoric acid.

To sum up, for *separate* estimations, in a superphosphate or in a manure, of phosphoric acid soluble in water and the same soluble in citrate of ammonia, it is better to estimate the phosphoric acid soluble in water *directly*, the phosphoric acid soluble both in water and citrate of ammonia *together*, and the phosphoric acid soluble in citrate of ammonia only *by difference.—Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 20-21.

THE PURIFICATION OF ACETYLENE.

By P. WOLFF.

Hardly a day passes without some new method for the purification of acetylene being proposed with the object of preventing the formation of smoke, which always accompanies the combustion of this gas. This smoke is due to the polymerisation of the acetylene itself; it can therefore only be prevented by using special burners, and not by further purifying an already sufficiently pure gas.

Ferric hydrate, Laming's mixture, or any other analogous product, can be used for absorbing the ammonia and the sulphuretted hydrogen; but they do not absorb the phosphoretted hydrogen, which really constitutes the only objectionable impurity. To absorb this gas, Lunge and Cedercreutz have proposed the use of chloride of lime, which plays the part of an oxidising agent (*Journ. Soc. Chem. Ind.*, 1897, p. 1046).

Now, previous experiments showed the author that the action of chloride of lime on acetylene is accompanied by small explosions, following the formation of chloride of nitrogen at the expense of the chlorine of the chloride of lime and of the nitrogen of the ammonia which is always to be found in acetylene. It is therefore necessary to free the acetylene of its ammonia before purifying it with chloride of lime. This can be thoroughly done by simply washing with water. Chloride of lime can absorb phosphide of hydrogen at the same time as the sulphydric gas without danger. Thus purified, acetylene possesses only a faint ethereal odour, which should, if possible, be accentuated, for facilitating the detection of leaks. This can be effected by mixing with it a small quantity of carbylamine or acetate of amyl, or, again, by simply passing it over carbide of calcium. The act of drying by contact with this body causes the liberation of a small quantity of raw acetylene, which communicates sufficient smell without contaminating it to any appreciable extent.

Pure acetylene does not attack copper or its alloys, but any trace of impurities quickly causes brown stains to appear on polished bronze ornaments. These stains are formed of phosphide, and not acetylide, of copper.—*Chemiker Zeitung*, xxii., [28], p. 281.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending January 31st, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 10th, 1899.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month, all were found to be clear, bright, and well filtered.

There has been a considerable excess of rain during during January, the actual fall at Oxford was 2·85 inches, the average fall for the past thirty years is 2·16 inches; this gives an excess of 0·69 inch, or 31·9 per cent.

Our bacteriological examinations of 255 samples have given the results recorded in the following table; we have also examined 37 other samples, from special wells, standpipes, &c., making a total of 292 samples in all :—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	1651
New River, filtered (mean of 25 samples) ..	11
Thames, unfiltered (mean of 25 samples) ..	22764
Thames water, from the clear water wells of five Thames-derived supplies (mean of 128 samples)	35
Ditto ditto .. .. highest	260
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	4576
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	14

The above figures show the average bacteriological condition of the London waters to be highly satisfactory, being only 35 microbes per cubic centimetre although the crude Thames water contained upwards of 22,000 per c.c.; this shows a very high efficiency of filtration. It will be observed that one sample gave an abnormal result, namely, 260 microbes per c.c. This was caused by a temporary defect in a filter, which was immediately detected by us, and at once attended to.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

DERIVATIVES OF THE TETRABROMIDES OF ZIRCONIUM AND THORIUM.*

By J. MERRITT MATTHEWS.

1.—Introduction.

This investigation was taken up as an adjunct to a preceding research (*Journ. Am. Chem. Soc.*, xx., p. 815; Chem. News, lxxix., p. 6) on the Derivatives of the Tetrachlorides.

Only derivatives with the four most typical amines—ammonia, ethylamine, aniline, and pyridine—were prepared, as it was considered needless to extend the investigation further, when the aim was only to prove a general reaction between the amine bases and the tetrahalides of the fourth group.

The anhydrous tetrabromides of zirconium and thorium were prepared in a manner exactly similar to their tetrachlorides, dry bromine vapours in a current of carbon dioxide gas being substituted for chlorine (Mellis, *Ztschr. Chem.*, [2], vi., 296; Troost and Ouvrard, *Ann. Chim. Phys.*, [6], xvii., 229).

Owing to the slight solubility of the tetrabromides in any of the usual organic solvents, the reagents in all cases were added to the dry salts, any excess being removed by washing the product so formed with ether.

Several attempts were made to prepare the tetrabromide of lead, proceeding in a manner analogous to that used in the preparation of the tetrachloride, but without success.

2.—The Amine Derivatives.

A. *Ammonia.*

a. Zirconium Tetrabromide, $ZrBr_4.4NH_3$.—On passing dry ammonia gas over zirconium tetrabromide at a slightly elevated temperature, a white compound was formed.

0·5186 grm, zirconium tetrabromide increased in weight to 0·6035 grm.

0·2246 grm. of this compound on analysis gave:—

0·3511 grm. silver bromide = 0·1494 grm. bromine = 66·50 per cent bromine.

0·0584 grm. zirconium dioxide = 0·0432 grm. zirconium = 19·22 per cent zirconium.

0·3024 grm. material gave:—

0·2426 grm. platinum = 0·0422 grm. ammonia = 13·96 per cent ammonia.

	Calculated for $ZrBr_4.4NH_3$.	Found.
Bromine	66·80	66·50
Zirconium	18·96	19·22
Ammonia	14·23	13 96
	Grm.	Grm.
Increase in weight	0·0861	0·0849

b. Thorium Tetrabromide, $ThBr_4.3NH_3$.—This was prepared in the same manner as the zirconium compound, and was white in colour.

0·4712 grm. thorium tetrabromide increased in weight to 0·5119 grm., which on analysis gave:—

0·6491 grm. silver bromide = 0·2762 grm. bromine = 53·96 per cent bromine.

0·2273 grm. thorium dioxide = 0·1997 grm. thorium = 39·01 per cent thorium.

	Calculated for $ThBr_4.3NH_3$.	Found.
Bromine	53·07	53·96
Thorium	38·47	39·01
	Grm.	Grm.
Increase in weight	0·0435	0·0407

B. *Ethylamine.*

a. Zirconium Tetrabromide, $ZrBr_4.4C_2H_5NH_2$.—0·2506 grm. zirconium tetrabromide, treated with ethylamine, gave 0·3572 grm. of a white compound, which on analysis yielded:—

0·4597 grm. silver bromide = 0·1956 grm. bromine = 54·75 per cent bromine.

0·0769 grm. zirconium dioxide = 0·0569 grm. zirconium = 15·92 per cent zirconium.

	Calculated for $ZrBr_4.4C_2H_5NH_2$.	Found.
Bromine	54·12	54·75
Zirconium	15·36	15 92
	Grm.	Grm.
Increase in weight	0·1098	0·1066

b. Thorium Tetrabromide, $ThBr_4.4C_2H_5NH_2$.—0·3121 grm. thorium tetrabromide, treated with ethylamine, gave 0·4098 grm. of a white compound which on analysis yielded:—

0·4246 grm. silver bromide = 0·1807 grm. bromine = 44·09 per cent bromine.

0·1502 grm. thorium dioxide = 0·1320 grm. thorium = 32·21 per cent thorium.

	Calculated for $ThBr_4.4C_2H_5NH_2$.	Found.
Bromine	43·71	44·09
Thorium	31·69	32·21
	Grm.	Grm.
Increase in weight	0·1018	0·0977

C. *Aniline.*

a. Zirconium Tetrabromide, $ZrBr_4.4C_6H_5NH_2$.—0·2075 grm. zirconium tetrabromide, treated with aniline, gave 0·4117 grm. of a brownish coloured compound which on analysis yielded:—

0·3821 grm. silver bromide = 0·1626 grm. bromine = 40·47 per cent bromine.

0·0631 grm. zirconium dioxide = 0·0467 grm. zirconium = 11·62 per cent zirconium.

	Calculated for $ZrBr_4.4C_6H_5NH_2$.	Found.
Bromine	40·83	40·47
Zirconium	11·46	11·62
	Grm.	Grm.
Increase in weight	0·1911	0·1932

b. Thorium Tetrabromide, $ThBr_4.4C_6H_5NH_2$.—0·2214 grm. thorium tetrabromide, treated with aniline, gave 0·3675 grm. of a brown coloured compound which on analysis yielded:—

0·3032 grm. silver bromide = 0·1290 grm. bromine = 35·10 per cent bromine.

0·1069 grm. thorium dioxide = 0·0939 grm. thorium = 25·56 per cent thorium.

	Calculated for $ThBr_4.4C_6H_5NH_2$.	Found.
Bromine	34·63	35·10
Thorium	25·11	25·56
	Grm.	Grm.
Increase in weight	0·1492	0·1461

D. *Pyridine.*

a. Zirconium Tetrabromide, $ZrBr_4.2C_5H_5N$.—0·3551 grm. zirconium tetrabromide, treated with pyridine, gave 0·3718 grm. of a brown compound which on analysis yielded:—

0·4876 grm. silver bromide = 0·2075 grm. bromine = 55·82 per cent bromine.

0·0802 grm. zirconium dioxide = 0·0604 grm. zirconium = 16·24 per cent zirconium.

	Calculated for $ZrBr_4.2C_5H_5N$.	Found.
Bromine	56 22	55·82
Zirconium	15·95	16·24
	Grm.	Grm.
Increase in weight	0·1357	0 1325

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xx., No. 11.

b. Thorium Tetrabromide, $ThBr_4.C_5H_5N$.—0·2817 grm. thorium tetrabromide, treated with pyridine, gave 0·3343 grm. of a brownish compound which on analysis yielded:—

0·3960 grm. silver bromide = 0·1685 grm. bromine = 50·42 per cent bromine.

0·1412 grm. thorium dioxide = 0·1241 grm. thorium = 37·11 per cent thorium.

	Calculated for $ThBr_4.C_5H_5N$.	Found.
Bromine	50·71	50·42
Thorium	36·77	37·11
	Grm.	Grm.
Increase in weight	0·0403	0·0426

It will be noticed that these derivatives of the tetrabromides correspond very closely to those of the tetrachlorides of these same elements in the number of molecules of the amine in combination with one molecule of the halogen salt.

It may be remarked that Classen and Zahorski (*Zeit. Anorg. Chem.*, iv, 100) have obtained additive compounds of lead tetrabromide and lead tetraiodide with the hydrobromic and hydriodic acid salts of several of the organic amines, by decomposing the corresponding chlorine compounds with cooled solutions of potassium bromide or potassium iodide. Thus, $PbCl_4.2(C_9H_7N.HCl)$ with potassium bromide gave $PbBr_4.2(C_9H_7N.HBr)$, and with potassium iodide $PbI_4.2(C_9H_7N.HI)$.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 2nd, 1899.

Professor DEWAR, F.R.S., President, in the Chair.

(Concluded from p. 81).

*17. "*The Chemistry of the so-called Nitrogen Iodide.*" Part I.—"*The Preparation and Properties of Nitrogen Iodide.*" By F. D. CHATTAWAY and K. J. P. ORTON.

Well-defined crystals of nitrogen iodide have been obtained by several new reactions. They are best produced by adding ammonia to a solution of potassium hypoiodite containing 0·02 grm.-molecule per litre. The liquid, after remaining clear for about half a minute, slowly deposits glittering needles, which are copper-coloured by reflected and red by transmitted light. These crystals have a specific gravity of 3·5, are dichroic, and probably belong to the orthorhombic system.

Part II.—"*The Action of Reducing Agents on Nitrogen Iodide.*" By F. D. CHATTAWAY and H. P. STEVENS.

All ordinary reducing agents rapidly decompose nitrogen iodide being themselves oxidised, whilst hydrogen iodide and ammonia are formed. The quantity of reducing agent oxidised is found in every case to be exactly double the amount equivalent to the hydrogen iodide produced.

The results obtained by the use of sodium sulphite, sulphurous acid, arsenious oxide, antimonious oxide, stannous chloride, and hydrogen sulphide are given in the following table:—

Amount of reducing agent oxidised:—	Na_2SO_3	H_2SO_3	As_2O_3	Sb_2O_3	$SnCl_2$	H_2S
Amount of hydriodic acid simultaneously produced —	HI	HI	2HI	2HI	HI	HI

The iodine contained in nitrogen iodide, therefore, behaves towards reducing agents like the chlorine contained in a hypochlorite, and exerts twice its normal oxidising action.

Part III.—"*The Composition of Nitrogen Iodide.*" By F. D. CHATTAWAY.

Scarcely any of the numerous published analyses of nitrogen iodide agree, those of the same observer often differing widely. It is usually stated that a number of distinct compounds exist, but this statement is based entirely on these discordant results, and is unjustifiable, for in no case has the substance analysed been shown to be pure, and in no case has the reaction on which the analysis is based been thoroughly studied; two reactions, indeed, must always have occurred, one of which has been overlooked. A method of analysis has now been investigated, and the conditions necessary for a single reaction to take place determined. By means of this method, specimens prepared by every reaction known to yield nitrogen iodide have been analysed, weighed quantities of the dry substances being employed in all important cases.

It is thus proved that only one compound exists, and that this has a composition represented by the formula $N_2H_3I_3$. The molecular weight and the manner in which the atoms are linked together remain to be settled by further investigation.

Part IV.—"*The Action of Light on Nitrogen Iodide.*" By F. D. CHATTAWAY and K. J. P. ORTON.

Nitrogen iodide suspended in ammonia is decomposed both by sunlight and by artificial light, forming nitrogen and hydrogen iodide, the latter being neutralised by the ammonia, $N_2H_3I_3 = N_2 + 3HI$. At the same time, a very small quantity of the compound is hydrolysed, ammonia and ammonium hypoiodite being formed,—

$$N_2H_3I_3 + 3H_2O = 2NH_3 + 3HOI;\ 2NH_3 + 3HOI + NH_3 = 3NH_4OI.$$

The ammonium hypoiodite, being somewhat unstable, slowly changes into ammonium iodide and ammonium iodate, $3NH_4OI = 2NH_4I + NH_4IO_3$.

Similar actions take place when nitrogen iodide suspended in water is exposed to light, and further, the hypoiodous acid and a portion of the hydrogen iodide interact, with the result that nitrogen is evolved, and iodine, hydrogen iodide, and ammonium iodide are formed. Powdered iodine, when placed in ammonia and exposed to light, is partially converted into nitrogen iodide, which then reacts normally.

Part V.—"*The Action of Alkaline Hydrates, of Water, and of Hydrogen Peroxide on Nitrogen Iodide.*" By F. D. CHATTAWAY and K. J. P. ORTON,

Solutions of alkaline hydrates rapidly decompose nitrogen iodide, two reactions simultaneously occurring even when light is completely excluded.

The chief reaction is one of hydrolysis, ammonia and an alkaline hypoiodite being produced. These hypoiodites, however, are unstable, and more or less rapidly change into iodides and iodates. The equations representing the action of potassium hydroxide, for example, are—

$$N_2H_3I_3 + 3KOH = 2NH_3 + 3KOI = 2NH_3 + 2KI + KIO_3.$$

At the same time, a portion of the nitrogen iodide always breaks down exactly as under the influence of light (preceding abstract), yielding nitrogen and hydrogen iodide, which combines with the base forming the iodide. Solutions of ammonia or hydroxides of the alkaline earth metals act similarly.

Water causes an analogous decomposition, but in this case the hypoiodous acid formed in the hydrolysis decomposes the hydrogen iodide produced, liberating iodine. The action of water on nitrogen iodide is rendered more rapid by the presence of basic oxides, and of salts, such as iodides and carbonates, which can combine or react with the hypoiodous and hydriodic acids formed.

Hydrogen peroxide dissolved in a solution of potassium hydrate rapidly decomposes nitrogen iodide, ammonia, potassium iodide, and a trace of potassium iodate being produced, whilst oxygen mixed with a little nitrogen is

evolved. The nitrogen iodide first reacts with the potash as if it alone were present, being hydrolysed to ammonia and potassium hypoiodite, but at the same time breaking down partially into nitrogen and hydrogen iodide. A very small quanity of the hypoiodite is transformed into iodide and iodate, but the greater part reacts with the hydrogen peroxide, liberating oxygen and being converted into iodide thus: $KOI+H_2O_2=KI+O_2+H_2O$. If a solution of hydrogen peroxide alone be added to nitrogen iodide, the water hydrolyses the compound and a similar action ensues, whilst iodine is set free by a further action of hydrogen peroxide on the hydrogen iodide remaining uncombined.

Part VI.—"*The Action of Acids on Nitrogen Iodide.*" By F. D. Chattaway and H. P. Stevens.

Dilute acids, when added to nitrogen iodide suspended in water, first induce hydrolysis of the compound, hypoiodous acid is liberated together with ammonia, which combines with the acid added—

$$N_2H_3I_3+\text{acid}+3H_2O=(2NH_3+\text{acid})+3HOI.$$

The further action depends on the nature of the acid used. If acids be employed such as sulphuric, phosphoric, boric, or acetic, on which hypoiodous acid has no effect, a rapid change into hydrogen iodide and iodic acid occurs, the former being immediately oxidised by a portion of the latter and iodine liberated,—

$$15HOI=10HI+5HIO_3=6I_2+6H_2O+3HIO_3.$$

If, however, the acid used reacts with hypoiodous acid, decomposition occurs, the nature of the final products depending on the acid employed. With hydriodic acid, for example, iodine is liberated, one half coming from the nitrogen iodide and one half from the acid,—

$$HOI+HI=I_2+H_2O;$$

with hydrochloric acid, iodine monochloride is produced, $HOI+HCl=ICl+H_2O$; whilst with hydrocyanic acid cyanogen iodide is formed, $HOI+HNC=INC+H_2O$.

In addition to this main action, it is found that when any acid except hydriodic or hydrocyanic acid is added to nitrogen iodide, light being excluded, a variable amount, depending on the strength of the acid, &c., decomposes exactly as it does under the influence of light, yielding nitrogen and hydrogen iodide; this hydrogen iodide then reacts with some of the hypoiodous acid formed in the hydrolysis, liberating iodine.

Part VII.—"*Theory of the Formation and Reactions of Nitrogen Iodide.*" By F. D. Chattaway and K. J. P. Orton.

In the formation of nitrogen iodide from iodine and aqueous ammonia, the iodine is first converted into equivalent quantities of ammonium iodide and ammonium hypoiodite, $I_2+2NH_4OH=NH_4I+NH_4OI+H_2O$; the greater part of the latter is then transformed into nitrogen iodide, which separates as a solid,—

$$3NH_4OI=N_2H_3I_3+NH_4OH+2H_2O,$$

but a small portion always remains unchanged. With iodine monochloride similar actions occur, ammonium chloride and hypoiodite being, however, the first products, $ICl+2NH_4OH=NH_4Cl+NH_4OI+H_2O$. If a solution of sodium or potassium hypoiodite be treated with a solution of ammonia, a partial conversion into the ammonium salt precedes the deposition of nitrogen iodide,—

$$KOI+NH_4OH=NH_4OI+KOH.$$

Solutions of ammonia kept in contact with nitrogen iodide are found to contain ammonium hypoiodite, the concentration increasing with the concentration of the ammonia and with the temperature. Nitrogen iodide is therefore formed from ammonium hypoiodite by a reversible action. This is found to be in accordance with the law of mass action if the concentration of the electrolytically dissociated ammonium hydroxide, NH_4OH, and not the total concentration of the ammonia, NH_3, be considered.

The experimental evidence so far seems to point to the conclusion that nitrogen iodide bears to ammonium hypoiodite a relation similar to that which the amide bears to the ammonium salt of an acid. The constitution of the compound, however, is still doubtful. The simplest explanation of its chemical behaviour is found in formulæ such as NH_3,NI_3 or NH_2I,NHI_2, whica represent each iodine atom as monovalent and directly connected with nitrogen. It is certain that neither iodine nor hydrogen iodide is present in loose molecular combination such as occurs in periodides or acid iodides.

Discussion.

Dr. Armstrong pointed out that, from an indexer's point of view, it was most important not to multiply papers unduly, and expressed the opinion that the four papers submitted by Messrs. Chattaway and Orton should be entered under the one simple title, "Nitrogen Iodide"; only two entries would then be required, in place of eight, in the authors' index.

In view of Dr. Chattaway's explanation that the error in the analyses communicated in his previous paper was due to exposure to light, it was worth noting, perhaps, that chemists were not sufficiently careful in excluding light: for years past he had been in the habit of brominating benzenoid hydrocarbons in the photographic dark room, with the result that products were obtained which were entirely free from the irritating odour of benzyl derivatives, and might be taken into a drawing-room without hesitation.

Dr. Scott referred to the much larger yield obtained when the iodine employed was dissolved in a solution of potassium iodide, and asked whether the substance so prepared was free from potassium compounds, and, bearing in mind Bunsen's formula, NH_3,NI_3, for nitrogen iodide, whether it was not probable that some, or even the whole, of the NH_3 might be replaced by compounds such as KI, giving rise to substances such as KI,NI_3. He also pointed out that none of the reactions described by the authors accounted for the large quantity of iodine set free when nitrogen iodide was treated with water at a temperature of 50—60°, a process employed by Stas for the preparation of pure iodine in large quantity and with perfect safety.

The President remarked that Guyard had suggested the employment of nitrogen iodide as an actinometer, so that the decomposition in light had been observed already. This decomposition was interesting, as it led to the inference that the iodide was an endothermic substance.

Dr. Chattaway, in reply, said that a full reference to Guyard's work was given in the paper. The authors were of opinion that they had settled finally the composition of nitrogen iodide, because every analysis made subsequent to the recognition of the causes of error confirmed it. The whole behaviour of the substance was in complete accord with this composition, and every reaction could be interpreted quantitatively.

The authors' results explained completely Stas's process for the purification of iodine. When nitrogen iodide is decomposed by water, two reactions had been shown to occur simultaneously and to an approximately equal extent: a part hydrolysed forming hypoiodous acid and ammonia, a part decomposed into hydrogen iodide and nitrogen, and the hydrogen iodide and hypoiodous acid interacted, liberating 90—95 per cent of the total iodine. Slight explosions, however, were always liable to occur, and the process consequently was dangerous. No evidence had been obtained of the existence of potassium compounds such as those suggested by Dr. Scott.

18. "*An Isomeride of Amarine.*" By H. Lloyd Snape, D.Sc., Ph.D., and Arthur Brooke, Ph.D.

From the distillation products, and also from the mother-liquors obtained by the action of ammonium cyanide upon benzaldehyde, the authors have isolated a new base isomeric with amarine and melting at 198°. It

forms salts with 1 equivalent of acids, forms a silver derivative containing 1 atomic proportion of the metal, and by distillation yields lophine.

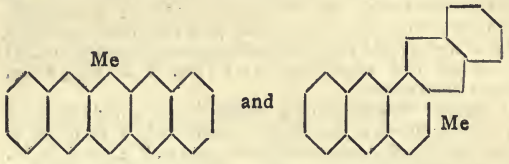
19. "*The Action of Chlorosulphonic Acid on Paraffins and other Hydrocarbons.*" By Sydney Young, D.Sc., F.R.S.

In a paper by Dr. F. E. Francis and the author (*Trans.*, 1898, lxxiii., 932) it was shown that fuming nitric acid, at the temperature of a water-bath, acts far less energetically on normal paraffins than on iso-paraffins, methyl derivatives of the polymethylenes or aromatic hydrocarbons, and that, generally, the action is more rapid on hydrocarbons which contain a CH-group than on others.

Similar results have now been obtained with chlorosulphonic acid at the ordinary temperature, and it is shown that this reagent may be used for removing small quantities of isoparaffins and methyl derivatives of the polymethylenes from the normal paraffins separated from petroleum by fractional distillation.

29. "*Derivatives of Dibenzylmesitylene.*" By W. H. Mills and Thomas H. Easterfield.

With the object of sythesising hydrocarbons of the types—



the authors have studied the benzoylation of mesitylene. Dibenzoylmesitylene has been described by Louise (*Ann. Chim. Phys.*, 1885, [vi.], vi., 191), but its isolation is difficult under the conditions employed by him. A good yield of the compound is obtained, however, by the interaction of benzoyl chloride with mesitylene at low temperatures in presence of much aluminium chloride. It is readily reduced by zinc dust and alcoholic potash, forming dihydroxydibenzylmesitylene, $C_6HMe_3(CHPh{\cdot}OH)_2$, a thick oil boiling at 326—330° at 50 m.m. pressure.

Dibenzylmesitylene is obtained from the secondary alcohol by prolonged reduction with zinc dust and alcoholic potash, or, more conveniently, by boiling the diketone with hydriodic acid and phosphorus. Dibenzylmesitylene is sparingly soluble in cold, easily in hot alcohol, from which it crystallises in well-defined prisms. It melts at 89° and boils at 280° under a pressure of 30 m.m. Its vapour density agrees with that required for the formula $C_{23}H_{24}$. This dibenzylmesitylene differs from that described by Louise (*loc. cit.*), which melted at 131° and was sparingly soluble in hot alcohol. It is not improbable that the latter is a tribenzylmesitylene, and, as analysis alone cannot settle this point, Louise's experiments are being repeated.

When dibenzoylmesitylene is oxidised in sealed tubes with dilute nitric acid at 140°, it is almost completely converted into two isomeric *dibenzoyluvitic acids*; a small quantity of *dibenzoylmesitylenic* acid is formed at the same time. The latter may be precipitated from a solution of the mixed sodium salts and sodium acetate by dilute acetic acid, and the uvitic acids from the mother-liquor by hydrochloric acid. On treatment with methylic alcohol and hydrogen chloride, the crude dibenzoyluvitic acids yield two isomeric methylic salts. One of these is crystalline, melts at 248°, and is sparingly soluble in alcohol; the other is oily and easily soluble. On hydrolysis, the crystalline ethereal salt yields an acid melting at 262°; the isomeric acid from the oily salt melts at 210°. The acid of higher melting-point is the more easily etherified.

The mixture of dibenzoyluvitic acids is oxidised by alkaline permanganate to a *dibenzoyltrimesic* acid, which crystallises from dilute hydrochloric acid in minute rosettes melting at 245°. Its salts, with the exception of the silver, copper, lead, and ferric compounds, are easily soluble.

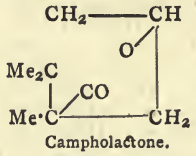
The action of condensing agents on these compounds is being investigated.

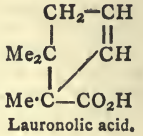
21. "*On Pseudocampholactone and Pseudolauronolic Acid.*" By Frederick H. Lees and W. H. Perkin, Jun.

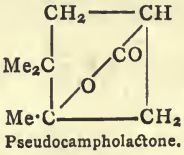
In a previous communication (*Proc.*, 1898, xiv., 111) the authors showed that, when camphoric anhydride is treated in chloroform solution with aluminium chloride at ordinary temperature, there is formed, besides isolauronolic acid, a new lactone, $C_9H_{14}O_2$, isomeric with campholactone and named pseudocampholactone. On hydrolysing this with baryta, a syrupy acid, $C_9H_{16}O_3$, was obtained; this eventually solidified, and has been found to consist of two isomeric acids, $C_9H_{16}O_3$, melting respectively at 109° and 152°.

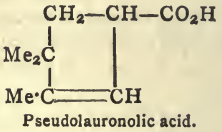
Pseudocampholactone readily interacts with phosphorus pentabromide, and, on pouring the product into methylic alcohol, *methylic bromodihydro-ψ-lauronolate*, $C_8H_{14}Br{\cdot}CO_2Me$, is obtained; this boils at 160—165° at 35 m.m., and when digested with diethylaniline yields *methylic-ψ-lauronolate*, which boils at 212—213° at 751 m.m. pressure.

ψ-Lauronolic acid, $C_8H_{13}{\cdot}CO_2H$, obtained by hydrolysing its methylic salt, is a colourless oil boiling at 147—149° at 20 m.m.; it is slightly lævorotatory and is an unsaturated acid, as its solution in sodium carbonate instantly reduces permanganate. On digestion with 33 per cent sulphuric acid, it is converted into pseudocampholactone. This new acid is of special interest, because it is isomeric with lauronolic, isolauronolic, campholytic, and allocampholytic acids, and the authors consider it probable that the relationship between campholactone and lauronolic acid, and pseudocampholactone and pseudolauronolic acid, may be represented by the formulæ—


Campholactone.


Lauronolic acid.


Pseudocampholactone.


Pseudolauronolic acid.

Isolauronolic acid is not obtained when a solution of camphoric anhydride in chloroform is left in contact with aluminium chloride for several days, but in its place two new acids are formed—a crystalline saturated acid, $C_9H_{16}O_2$, melting at 76—77°, and a liquid unsaturated acid. These acids, as well as ψ-lauronolic acid, are being submitted to careful investigation, the results of which the authors hope soon to be able to communicate to the Society.

22. "*Nitrocamphor as an example of Dynamic Isomerism.*" By T. Martin Lowry, B.Sc.

As has been pointed out in a previous communication (*Proc.*, 1898, xiv., 152), the rotatory power of both nitrocamphor and π-bromonitrocamphor varies, not only when different solvents are used, but also with time, and this may be regarded as proof that the normal and pseudo-forms of these substances are isodynamic, the change of structure being attended with a change of rotatory power in the freshly-prepared solutions. The change of rotatory power of nitrocamphor has been studied in fifteen different solvents; it usually extends over a period of a few hours or days, but at higher temperatures, or in presence of a trace of piperidine or of sodium ethylate, takes place

almost instantaneously; on the other hand, a solution in chloroform can often be kept in a labile state during several days, which is perhaps an indication that the change is due to the presence of some third substance. Equilibrium is reached in the case of both nitrocamphor and π-bromonitrocamphor when about 6 per cent of the substance in solution is in the pseudo-form.

The author advances the opinion that the changes of rotatory power which take place in freshly-prepared solutions of many of the sugars are also due to the occurrence of isodynamic change, and not to the formation of hydrates, as has usually been assumed. In the case of glucose and of lactose, both isodynamic forms appear to have been isolated in an anhydrous state; when dissolved in water they pass to a condition of equilibrium in exactly the same manner as has been found to be the case with the isodynamic forms of π-bromonitrocamphor.

The bearing of the observations made with nitrocamphor on the general problem of dynamic isomerism is discussed in the concluding sections of the paper. The author hopes to extend this method of investigation to cyanocamphor and isonitrosocamphor, and to other optically active substances which may conceivably give rise to dynamic isomerides.

23. "*Position-isomerism and Optical Activity; the Methylic and Ethylic Salts of Benzoyl- and of Ortho-, Meta-, and Para-toluylmalic Acid.*" By Percy Frankland, F.R.S., and Frederick Malcolm Wharton.

In continuance of their work on the influence of position-isomerism on optical activity, the authors have prepared and examined the following compounds. The rotation of each compound was determined at temperatures ranging from 20—137°. The results may be summarised as follows (see Table).

Methylic Malate.

d	20°/4° = 1·2301	$[\alpha]_D$ 20°	= −6·84°

Methylic Benzoylmalate.

d	21°/4° = 1·2121	$[\alpha]_D$ 21°	= −5·62°
d	99°/4° = 1·1395	$[\alpha]_D$ 99°	= −11·56°
d	137·5°/4° = 1·1037	$[\alpha]_D$ 137·5°	= −13·64°

Methylic Orthololuylmalate.

d	23°/4° = 1·1909	$[\alpha]_D$	= −8·94°
d	98°/4° = 1·1181	$[\alpha]_D$ 98°	= −12·40°
d	135°/4° = 1·0822	$[\alpha]_D$ 135°	= −14·09°

Methylic Metatoluylmalate.

d	20°/4° = 1·1925	$[\alpha]_D$ 20°	= −6·34°
d	99°/4° = 1·1127	$[\alpha]_D$ 99°	= −11·73°
d	136°/4° = 1·0753	$[\alpha]_D$ 136°	= −13·49°

Methylic Paratoluylmalate.

d	18·5°/4° = 1·1957	$[\alpha]_D$ 18·5°	= −3·14°
d	99°/4° = 1·1088	$[\alpha]_D$ 99°	= −8·33°
d	136°/4° = 1·0688	$[\alpha]_D$ 136°	= −10·14°

Ethylic Malate.

d	20°/4° = 1·1340	$[\alpha]_D$ 20°	= −10·44°

Ethylic Benzoylmalate.

d	21°/4° = 1·1561	$[\alpha]_D$ 21°	= −3·87°
d	98°/4° = 1·0759	$[\alpha]_D$ 98°	= −9·84°
d	137°/4° = 1·0349	$[\alpha]_D$ 137°	= −12·08°

Ethylic Orthotoluylmalate.

d	21°/4° = 1·1391	$[\alpha]_D$ 21°	= −6·25°
d	100°/4° = 1·0714	$[\alpha]_D$ 100°	= −10·38°
d	136°/4° = 1·0405	$[\alpha]_D$ 136°	= −12·01°

Ethylic Metatoluylmalate.

d	21°/4° = 1·1371	$[\alpha]_D$ 21°	= −4·67°
d	99·5°/4° = 1·0603	$[\alpha]_D$ 99·5°	= −9·93°
d	137·5°/4° = 1·0229	$[\alpha]_D$ 137·5°	= −11 66°

Ethylic Paratoluylmalate.

d	20°/4° = 1·1382	$[\alpha]_D$ 20°	= −0·22°
d	99°/4° = 1·0513	$[\alpha]_D$ 99°	= −5·55°
d	136°/4° = 1·0106	$[\alpha]_D$ 136°	= −7·31°

Thus the lævorotation of ethylic malate is diminished by the introduction of all the acidyl groups in question. The lævorotation of methylic malate is also depressed by the introduction of the benzoyl, meta- and para-toluyl groups, but raised by that of the orthotoluyl group. At 20° the depressing, or dextrotatory, influence of the several groups follows in the order, para-toluyl > benzoyl > metatoluyl > orthotoluyl, both in the case of the methylic and ethylic compounds. At a high temperature (136°), on the other hand, the sequence of the dextrorotatory influences of these groups is parotoluyl > metatoluyl > benzoyl > orthotoluyl in the case of methylic malate, and paratoluyl > metatoluyl > orthotoluyl or benzoyl (practically identical) in the case of ethylic malate. In all cases, therefore, the dextrorotatory influence of the acidyl groups in question is more pronounced on the ethylic than on the methylic compound.

24. "*Some Regularities in the Rotatory Power of Homologous Series of Optically Active Compounds.*" By Percy Frankland, F.R.S.

The author endeavours to explain the results obtained in the previous paper (Percy Frankland and Wharton) by adducing evidence that methylic and ethylic malates both exist as associated molecules, and that methylic is more associated than ethylic malate. It is suggested that the lower lævorotation of methylic as compared with that of ethylic malate is due to the greater degree of association of the former, and that, in the unassociated state, the lævorotation of the methylic salt would be the greater. The acidyl-malates are probably much less, if not entirely, unassociated, hence the invariably greater lævorotation of the methylic acidyl-malate as compared with that of the corresponding ethylic derivative. The author reviews a large number of other homologous series of optically active compounds, and investigates the degree of association of each term with the aid of Traube's method of calculating molecular volume. From this investigation it would appear that the striking phenomenon of a maximum rotation occurring within an homologous series may probably be accounted for, in some cases, by the greater degree of association occurring in the initial terms, this association leading to the rotatory power actually observed being less than that possessed by the unassociated substance. In such cases, when a substitution is effected which does away with association, the maximum rotation within the series also disappears. Thus the malates exhibit a maximum rotation at the propylic term, whilst in the substituted malates the maximum disappears. In other cases the existence of a well-defined maximum rotation within an homologous series would not appear to admit of explanation in this manner. Such maxima occur in all well-authenticated cases at about the butylic term of the homologous series, and the author suggests that this may be due to stereochemical causes, as the occurrence of some irregularity in the rotation might be anticipated at the point where a growing chain attached to the asymmetric carbon atom attains such a magnitude that the chain has doubled on itself,—that is, when it contains about 5 carbon atoms. It is suggested that the same stereochemical cause may affect other physical properties, and that the greater tendency to association of the initial terms of an homologous series may be dependent on space conditions.

25. "*On Brasilin and Hæmatoxylin.*" By A. W. Gilbody and W. H. Perkin, Jun.

During the last three years the authors have been investigating these important natural colouring-matters, and now give a short abstract of the results obtained, in order that they may reserve the further study of the various decomposition products which they have prepared for the first time.

Trimethylbrasilin, $OH{\cdot}C_{16}H_{10}O(OME)_3$, when oxidised under certain conditions with chromic acid, yields *trimethylbrasilone*, $OH{\cdot}C_{16}H_8O_2(OMe)_3$, which crystallises in straw-coloured needles, melts at 191°, and at a somewhat higher temperature loses $1H_2O$, forming *dehydrotrimethylbrasilone*, $OH{\cdot}C_{16}H_6O(OMe)_3$. This crystallises in colourless needles, melts at 198°, and when treated with acetic anhydride is converted into an *acetyl* compound, $OAc{\cdot}C_{16}H_6O(OMe)_3$, which melts at 176°, and is probably identical with the substance which Herzig (*Monats.*, 1895, xvi., 913) obtained by oxidising acetyltrimethyl brasilin.

Nitric acid oxidises trimethylbrasilone, forming nitroparamethoxysalicyilc acid (m. p. 232°) and a substance represented probably by the formula $C_{11}H_8O_5(OMe)_2$; the latter crystallises in yellow needles, yields an acetyl compound, reacts with phenylhydrazine and parabromophenylhydrazine, and is characterised by forming an intense purple solution in dilute alkalis. If this purple solution is gently warmed deecomposition sets in, with the production of paramethoxysalicylic acid (m. p. 157°) and two neutral substances which melt at 118° and 206°, and which, on analysis, give numbers agreeing with those required for the formulæ $C_{11}H_{14}O_6$ and $C_{12}H_{14}O_6$ respectively.

From the mother-liquors obtained during the preparation of trimethylbrasilone the following substances have been isolated in small quantities:—(*a*) A substance crystallising in colourless needles and melting at 183°; this has not yet been analysed. (*b*) A substance crystallising in colourless crystals, melting at 210°, and giving with ferric chloride an intense violet colouration; the analysis gave numbers agreeing with those required for the formula $C_9H_{10}O_5$. (*c*) A substance melting at 155°, which crystallises from water in colourless needles, and appears to be a lactone of the formula $C_{15}H_{16}O_6$. This lactone, on oxidation with permanganate, yields a dibasic acid, $C_{10}H_{10}O_3(CO_2H)_2$, which melts at 200—203° with decomposition, due to the formation of the anhydride. When this dibasic acid is heated with hydrochloric acid at 160° it is decomposed with elimination of carbon dioxide, and, on extracting the solution with ether, beautiful colourless prisms are obtained, which melt at 104°, and consist of pure catechol; it thus appears probable that, in addition to the resorcinol ring, brasilin contains that of catechol.

When trimethylbrasilin is oxidised with permanganate it yields an acid melting at 129·5°, which apparently has the constitution $C_{10}H_8O_3(OMe)(CO_2H)$, and which, on fusion with potash, gives an oil which shows all the characteristic reactions of resorcinol. This acid, on oxidation with sodium hypobromite, is converted into an acid represented probably by the formula $C_{10}H_{10}O_9$, and this, on further oxidation with permanganate, gives an acid, $C_8H_8O_6$, which melts at about 225° with decomposition.

When *tetramethylhæmatoxylin*, $OH{\cdot}C_{16}H_9O(OMe)_4$ is oxidised with chromic acid, it yields *tetramethylhæmatoxylone*, $OH{\cdot}C_{16}H_7O_2(OMe)_4$, which melts at about 170° with decomposition. When heated with acetic anhydride it yields *acetyldehydrotetramethylhæmatoxylone*,—

$$OAc{\cdot}C_{16}H_5O(OMe)_4,$$

which crystallises in colourless needles, melts at 194°, and is probably identical with a compound melting at 191—192°, which Herzig (*loc. cit.*) obtained by oxidising acetyltetramethylhæmatoxylin.

When oxidised with nitric acid tetramethylhæmatoxylone behaves in the same way as trimethylbrasilone, yielding a substance which crystallises in yellow needles, and dissolves in alkalis with a purple colour, This substance is being investigated, as also are several substances which have been obtained from the mother-liquors obtained during the preparation of tetramethylhæmatoxylone. One of the latter compounds crystallises from water in colourless needles, melts at 214°, and on analysis gives numbers agreeing with those required for the formula $C_9H_{10}O_5(CO_2H)_2$.

The authors hope, by the examination of all these new substances, to obtain results which will enable them to assign formulæ to brasilin and hæmatoxylin, and they are continuing the investigation with the aid of Mr. H. Hibbert, B.Sc., who has already afforded much assistance in examining tetramethylhæmatoxylone.

NOTICES OF BOOKS.

Physico-Chemical Methods. By Dr. J. Traube, Privat Docent in the Technical High School of Berlin. Authorised Translation by Willitt L. Hardin, Ph.D., Harrison Senior Fellow in Chemistry, University of Pennsylvania. Philadelphia: P. Blakiston's Son and Co. London: Kegan Paul, Trench, Trübner, and Co., Lim.

Fully recognising the importance of physico-chemical methods in chemical investigation, we are glad to see an English translation of this important work.

The book opens in the usual way by a description of the balance, and rules for adjusting and working with it. Methods for estimating the density of solids, liquids, and gases are given at length, including descriptions and illustrations of most of the standard forms of apparatus for this purpose; in fact, the book is really a compilation of the various forms of apparatus for physico-chemical analysis at present in use in Continential laboratories.

The illustrations are poor, and in some cases very bad (see p. 65, "The Thermostat").

The translator in some instances has scarcely done justice to the work, and some of the expressions used are open to criticism. On page 15 a ground glass stopper is twice called a *cork*. In another place reference is made to an "everywhere purchaseable turbine"; this being the only description of the apparatus. And in another place, in describing the adjustment of the Hüfner-Albrecht rhomb in the spectrophotometer, we are told that a prism is to be *shoved* into its place!

A passage, too, on page 77 giving the method of filling a pycnometer with mercury in determining the coefficient of expansion is very indifferently translated, and reads:—"By carefully heating and cooling the pycnometer whereby the mercury is slowly heated to boiling the vessel is completely filled."

These oversights, trivial though they appear, detract much from the value of the book.

Notes on Essential Oils. With Special reference to their Composition, Chemistry, and Analysis. By T. H. W. Idris, F.C.S. With Tables of Constants of the more commonly occurring Oils. London and Bristol: Geo. Du Boistel and Co.

This little book will be found of great practical value to those working in essential oils. Not intended as a text-book, the details of analytical processes are omitted, but at the same time much practical information is given that is not at all likely to be found in an ordinary text-book.

In Chapter I., dealing with the camphor group, the obscurity of the chemistry of this group of compounds is pointed out, but a good outline of the most trustworthy data is given from the works of Bredt, Tiemann, Perkin, and others.

In the essential oils, the increasingly important oil of eucalyptus is briefly but clearly described, and some practical notes on methods of analysis are given, concluding with a table of specific gravity, optical rotation, and constituents of the oils from some fourteen species of eucalyptus.

The book concludes with a Table of Constants, giving the source, specific gravity, optical rotation, &c., of essential oils arranged in alphabetical order.

There is a clearly printed table of contents, enabling the data of any oil to be found with a minimum amount of labour.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 2, January 9, 1899.

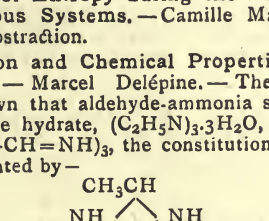
Preparation and Properties of Calcium Arsenide.—P. Lebeau.—The author has prepared in the electric furnace a crystallised arsenide of calcium with the formula As_2Ca_3, corresponding to the nitride N_2Ca_3. As in the case of the nitride and phosphide of calcium this arsenide decomposes water at ordinary temperatures, giving a gaseous hydride of formula AsH_3 and calcium hydrate. The arsenide prepared by the direct union of calcium and arsenic has exactly the same composition.

Decomposition of Carbonic Oxide in presence of Iron Oxide.—O. Boudouard.—The author's experiments show that the reaction of decomposition of carbonic oxide is a function of the time, and that it depends also on the quantity of iron oxide present. The amount of carbonic acid formed increases in a regular manner, and the decomposition ends by being total in the first two series of experiments, and no doubt the same result would be obtained in the third at the end of a sufficiently long time. The author investigates also the action of carbonic oxide in the presence of nickel and cobalt oxides at the same temperature of 445° and also at higher temperatures.

Volumetric Estimation of Cerium.—André Job.—A known weight of ammonium cerium nitrate is dissolved in nitric acid. The amount of oxide present per unit volume can be found by calcination. Dilute standard peroxide of hydrogen solution is run in until the nitrate is completely decolourised. By this means the amount of ceric cerium in acid solution can be estimated. From this the author deduces a method of estimating the total cerium present. He treats the cerium salt with binoxide of lead in the cold in presence of excess of nitric acid. The cerous salt is oxidised to ceric, and can be estimated volumetrically by the former method. This estimation can take place in the presence of thorium, lanthanum, and didymium.

Variation of Entropy during the Dissociation of Heterogeneous Systems.—Camille Matignon.—Not suitable for abstraction.

Constitution and Chemical Properties of Ethylidene-imine.—Marcel Delépine.—The author has formerly shown that aldehyde-ammonia should be considered as the hydrate, $(C_2H_5N)_3.3H_2O$, of ethylidene-imine, $(CH_3—CH=NH)_3$, the constitution of the latter being represented by—



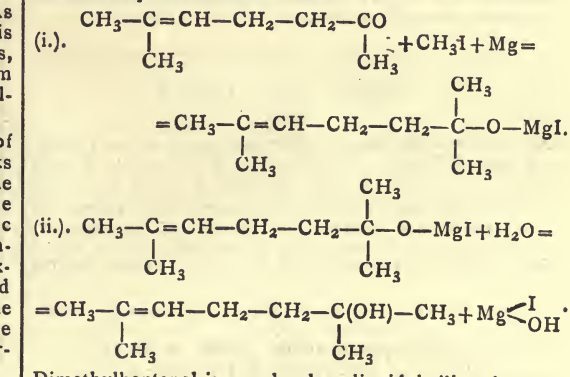
Facts are deduced in support of this formula. (1) The aldehyde-ammonia is a hydrate; ethylidene-imine being obtained from it when dried *in vacuo* over H_2SO_4. (2) One CH_3CH is joined to two N, as shown by the production of the body—

$$CH_3—CH\begin{matrix}NH.CO.C_6H_5\\NH.CO.C_6H_5\end{matrix}$$

when benzoyl chloride reacts with aldehyde-ammonia (3) The substance reacts as a secondary amine. (4) The molecule has a chain of six links.

Derivatives of Synthetic Methylheptenone.—Georges Leser.—The method of preparation of the ethyl ester of methylhexenone-pyruvic acid has been described. The corresponding acid is obtained by the action of sodium ethylate on methylheptenone and oxalic ether. The new acid is isolated, by precipitating with hydrochloric acid, in the form of colourless prisms melting at 39—50°, very soluble in most organic solvents. Analysis agrees with the formula $C_{10}H_{14}O_4$.

Synthesis of Dimethylheptenol.—Ph. Barbier.—One hundred grs. of natural methylheptenone, 150 grs. of anhydrous ether, and 20 grs. of magnesium turnings are placed in a flask, and 113 grs. of methyl iodide gradually added. The reaction is brisk, and the flask is cooled by a current of water. On addition of sulphuric acid, a liquid separates which is fractionated *in vacuo*. The reaction is represented as follows:—



Dimethylheptenol is a colourless liquid boiling between 79—80° under 10 m.m.

A Method of Formation of Urea.—A. Jouve.—The author has proved that a solution of carbon monoxide in ammoniacal cuprous chloride warmed to 105° for five or six hours gives urea. The reaction is expressed thus:—

$$(i.).\quad CO+(NH_3)_2=CO\begin{matrix}NH_2\\NH_2\end{matrix}+H_2,$$

$$(ii.).\quad Cu_2Cl_2+H_2=2HCl+Cu_2;$$

for, on the one hand, copper is deposited, and, on the other hand, the weight of metal formed and the weight of urea estimated by hypobromite are in the ratio indicated by these equations. The fatty and aromatic amines behave in an analogous manner. By dissolving cuprous chloride in dimethylamine and reacting with CO under pressure copper is formed, and probably also a urea; this has not yet been isolated.

MISCELLANEOUS.

On the Use of Acetylene as a Reagent in Quantitative Analysis.—H. G. Söderbaum.—*The Separation of Copper and Cadmium.*—The mixture of the two salts (0·5 to 0·8 grm.) is dissolved in about 150 cubic c.m. of water; 10 to 15 cubic c.m. of sulphurous and 20 to 25 cubic c.m. of ammonia of sp. gr. 0·96 are added. The solution is heated on the water-bath until it takes a

bright blue colour, and is then treated with a current of acetylene. The precipitate is washed several times by decantation with dilute ammonia saturated with acetylene, thrown on a filter, and washed with boiling water. The acetylide of copper thus obtained is heated with nitric acid, and the resulting nitrate is transformed into oxide by calcination, and then weighed. In the solution freed from acetylide of copper the cadmium is precipitated by ammonium sulphydrate, or else determined electrically after acidulation, and heating to drive off the sulphurous acid.

Separation of Copper and Arsenic.—If the arsenious or arsenic acid is in the form of an ammoniacal salt, the separation of the copper in the state of acetylide is incomplete, the precipitate always carrying down with it a certain proportion of arsenic. This inconvenience can be remedied by adding to the liquid a quantity of caustic soda sufficient to saturate the arsenious or arsenic acid. A current of acetylene is passed through the warm solution, until the precipitate collects easily and the liquid becomes clear. The filtrate is evaporated to dryness, the residue oxidised by nitric acid, and the resulting solution precipitated by magnesia mixture in the ordinary manner. The acetylene used in these operations should be washed with acetate of lead and acid bichloride of mercury; the object of using this latter is to absorb the phosphoretted hydrogen. In some experiments, when the acetylene was not washed with bichloride of mercury, the precipitate of acetylide of copper contained traces of phosphorus.—*Berichte*, xxx. [9], p. 3014.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Glass Specimen Bottles.—I shall be obliged if any reader of the CHEMICAL NEWS will inform me where stoppered bottles with feet can be obtained. They are, I believe, called "Rosebe" bottles.—W. C.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8 (Cantor Lectures). "Cycle Construction and Design," by Archibald Sharpe, A.M.Inst.C.E.

TUESDAY, 28th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

—— Society of Arts, 8. "Persian Trade Roules," by A. Hotz.

WEDNESDAY, March 1st.—Society of Arts, 8. "Leadless Glazes," by Wilton P. Rix.

THURSDAY, 2nd.—Royal Institution, 3. "Toxins and Antitoxins," by Dr. Allan Macfadyen, M.R.C.S.

—— Chemical, 8. "Brom-methylfurfuraldehyde," by H. J. H. Fenton and Mildred Gostling. B.Sc. "The Action of Metallic Thiocyanates on certain Substituted Carbamic and Oxamic Chlorides—and a New Method for the Production of Thiobiurets," by A. E. Dixon, M.D. "Ethylic $\beta\beta$-Dimethylpropanetetracarboxylate," by W. Trevor Lawrence. "The Reaction of Alkyl Iodides with Hydroxylamine—Formation of Alkylated Hydroxylamines and Oxamines," by Wyndham R. Dunstan, F.R.S., and John Goulding, B.Sc.

FRIDAY, 24th.—Royal Institution, 9. "King Alfred," by Sir Frederick Pollock, Bart., M.A., LL.D.

SATURDAY, 4th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2049.

THE FORMATION OF PERCHLORATES OF THE ALKALIS, AND OF THE ALKALINE EARTHS, BY ELECTROLYSIS.

By F. WINTELER.

THE prolonged electrolysis of the alkaline chlorides or of the alkaline earths in aqueous solution with platinum electrodes may give rise to the formation, not only of hypochlorites and chlorates, but also to that of perchlorates. In the short accounts which have already been published on the electrolytic transformation of chlorate of potassium into the perchlorate by means of platinum electrodes it is the more singular that none of the patents having for their object the electrolytic manufacture of chlorates take any notice of this phenomenon, and that the works quoted (Gmelin Kraus "Handbuch d. Anorg. Chem.," I. *a.*, p. 696; I. *b.*, p. 373; II. *a.*, p. 80; Gilbert's *Ann. Phys.*, 1816, lii., p. 218-219; *Journ. Prakt. Chem.*, 1847, xli., p. 138-139), have not been reproduced in any modern text-books.

When the electrolysis of the solutions of chlorides between the platinum electrodes has arrived at such a point that all the chloride is transformed into chlorate, the best conditions for the further oxidation of the chlorate into perchlorate are:—

1. The solution must be acid at the anode.
2. The temperature must be low at the anode.
3. The density of the current should be from 4 to 12 ampères per square decimetre.
4. The electrolyte should be a saturated solution.

If, for example, we electrolyse, without a diaphragm, a neutral solution of chlorate of potassium saturated at the ordinary temperature, with 8 ampères per square decimetre, taking care to maintain the temperature of the bath at 10° by means of a current of water, we find that at the commencement 73 per cent of the oxygen which should be disengaged is utilised in transforming the chlorate into perchlorate. A saturated solution of chlorate of sodium 1 : 1 gives under the same circumstances perchlorate of sodium with a return of 95 per cent. The return only commences to diminish at the moment when the chlorate is almost entirely oxidised; it then diminishes very rapidly.

It is of importance to cool the electrodes immediately. The apparatus should be constructed in such a manner that the electrodes are in contact with the electrolyte on one side only, otherwise the density of the current cannot be accurately measured. If, however, this condition cannot be fulfilled, the side of the anode facing the cathode is practically all that need be considered. The density of the current at the cathode may be arranged as we like, as it has no effect on the electromotive force of the current.

Reduction of the chlorate does not take place at all, even when we have to deal with a very feeble current. All conditions being equal, the best return is obtained with a current of from 8 to 12 ampères per square decimetre of the anode. The return is lowered if the density of the current is increased or diminished. Even solutions of chlorates containing 4 per cent of alkali furnish corresponding perchlorates, giving a return up to 10 per cent if the electrolyte at the anode and at the cathode is not disturbed except by the gas which is given off.

The formation of perchlorates is accompanied by the characteristic smell of ozone. A concentrated solution of chlorate and perchlorate gives off such large quantities of ozone that the indiarubber tubes and joints are reddened after only a few minutes. It would be worth while to carry out a research in this direction, with the object of preparing ozone industrially by means of electrolysis.

If carbon be used as the anode for the electrolysis of the chlorate, it is used up very rapidly without the formation of any perchlorate. The use of other metals than platinum and iridium is impossible on account of the formation of soluble salts with the anion ClO_3.

An interesting observation made by RICHE (*Comptes Rendus*, 1858, p. 348), and which of late years has passed unnoticed, is one relating to the formation of perchloric acid by the electrolysis of dilute hydrochloric acid between two platinum electrodes. According to my own experiments the most favourable conditions for this reaction are the same as those for the electrolytic preparation of the perchlorates. We obtain an acid the more concentrated as the temperature of the bath is lower. The temperature at which the chlorine remains entirely in solution is the most favourable. — *Chemiker Zeitung*, 1898, xxii., p. 90.

ON THE SEPARATION OF IRON FROM ZIRCONIUM AND CERTAIN OTHER ALLIED METALS.*

By J. MERRITT MATTHEWS.

THOUGH there have been several methods proposed in the past for the separation of iron from zirconium, still chemists have not considered that this problem has, as yet, been satisfactorily solved. All methods which have been recommended for the quantitative separation of these two metals have proved, in some particular, to be untrustworthy, for in all of them traces of iron appear to remain with the zirconium with great pertinacity.

As it may be of interest in connection with the present subject, a brief résumé will here be given of the principal methods which have hitherto been proposed for the separation of iron from zirconium.

Bailey (*Journ. Chem. Soc.*, xlix., 481), by the use of a moderately concentrated solution of hydrogen peroxide, precipitates Zr_2O_5, whereas neither iron, aluminum, nor titanium salts are precipitated by this reagent. No accurate results, however, have been worked out by this method.

Berlin (*Journ. Prakt. Chem.*, lviii., 147), observes that if zirconium dioxide, contaminated with iron, is fused with sodium carbonate to a white heat, and the fusion treated with hydrochloric acid, the iron salt dissolves, leaving the zirconium dioxide undissolved. Scheerer (*Pogg. Ann.*, lix,, 48), claims that by this fusion a sodium zirconate is formed at first, which is subsequently decomposed on washing with water. Some of the zirconium, however, will go into the solution with the iron; and, on the other hand, the zirconate dioxide will still be slightly contaminated with traces of ferric oxide.

Stromeyer (*Ann. Chem. Pharm.*, cxiii., 127), applies Chancel's method (*Journ. Prakt. Chem.*, lxxiv., 471), for the separation of iron from aluminum to its separation from zirconium. By boiling with sodium thiosulphate, zirconium hydroxide is precipitated, while the iron remains in solution. Hermann (*J. Pr. Chem.*, xcvii., 340), however, says that this procedure results in the formation of a zirconium hyposulphite; and traces of iron still continue with the zirconium. For an approximate separation, however, this seems to be a good one.

Rivot (*Ann. Chim. Phys.*, xvii., 244), recommends the reduction of the iron to the metallic condition, by heating in a current of hydrogen. But it is very doubtful if all of the iron will be eliminated from the zirconium dioxide by this means.

* *Journal of the American Chemical Society*, xx., No. 11, Nov., 1898.

Berthier (*Ann. Chem. Phys.*, l., 362), uses ammonium hydroxide and sulphide, which precipitates ferrous sulphide, FeS, and zirconium hydroxide, $Zr(OH)_4$; when this mixture is treated with sulphurous acid, the ferrous sulphide dissolves; the filtrate may contain some zirconium salt which, on heating, is precipitated from the iron as hydroxide. Hermann claims that this method does not give zirconium dioxide free from iron. Henneberg (*Journ. Prakt. Chem.*, xxxviii., 508), obtains a zirconium dioxide pure, except in that portion which is precipitated on heating.

Hermann claims to have obtained very pure zirconium dioxide by treating a solution of the chloride with a corresponding amount of ammonium oxalate, and igniting the precipitate. But in this method the amount of zirconium must be known beforehand, in order to calculate the quantity of ammonium oxalate to be added, as any excess of the latter reagent will dissolve the precipitate.

Dubois and Silveria observe that if impure zirconium hydroxide is boiled with oxalic acid, the iron oxalate formed is easily soluble, whereas the zirconium oxalate is insoluble. But Berlin (*Journ. Prakt. Chem.*, lviii., 145), found that the zirconium oxalate is somewhat soluble in oxalic acid, which fact vitiates this method.

Classen (*Ber. d. Chem. Ges.*, xiv., 2783), gives an electrolytic separation of iron from zirconium; but by his method the zirconium is only determined by difference.

Another method which has been recommended is to boil the impure zirconium salt with a solution of potassium sulphate, when a basic sulphate of zirconium will be precipitated. The precipitation, however, is never complete, as the filtrate always contains some of the zirconium.

It will be seen by this short review that the separation of iron from zirconium is by no means a positive certainty, as there seems to be a great many conflicting opinions entertained by the different authorities.

Details of the Method for the Separation of Iron from Zirconium.

On introducing a small quantity of water into an ethereal solution of zirconium tetrachloride, it was noticed that a white precipitate was formed, insoluble in excess of ether. This precipitate was no doubt an oxychloride of zirconium, and analysed in accordance with the well-known hydrated chloride, $ZrOCl_2{\cdot}8H_2O$.

I. 0·1682 grm. material gave:—

0·1492 grm. silver chloride = 21·93 per cent chlorine.
0·0645 grm. zirconium dioxide = 28·34 per cent zirconium.

II. 0·1276 grm. material gave:—

0·1181 grm. silver chloride = 21·86 per cent chlorine.
0·0488 grm. zirconium dioxide = 28·26 per cent zirconium.

	Calculated for $ZrOCl_2{\cdot}8H_2O$.	Found. I.	Found. II.
Chlorine	22·05	21·93	21·86
Zirconium	28·18	28·34	28·26

On testing this precipitate with a solution of potassium thiocyanate, not a trace of iron was indicated, although the zirconium tetrachloride used in the solution showed a decided contamination by iron under the same conditions.

With this sharp distinction in solubilities of the hydrated salts of zirconium and iron in ether as a basis, a simple and accurate separation of these two elements was immediately suggested.

Weighed quantities of the chlorides of zirconium and iron were mixed together. Previous analyses of these salts were made in order to determine their respective percentages of zirconium and iron. The mixed salts were dissolved in water and carefully evaporated to dryness on a water-bath; after cooling they were treated with absolute ether, and dry hydrochloric acid gas was passed through the liquid. Experience proved that this latter treatment was necessary to effect a rapid and complete solution of the iron salt by the ether, as the ferric chloride on evaporation to dryness evidently forms basic compounds of indefinite composition which are difficulty soluble in ether. The solution was rapidly filtered, and the residue washed with absolute ether several times to insure the removal of the last traces of the iron salt. The residue was then dissolved in water, and the zirconium determined by precipitation as hydroxide by means of ammonium hydroxide; drying the precipitate, igniting and weighing as zirconium dioxide, ZrO_2. The ether was evaporated or distilled from the filtrate, and the residue dissolved in water, with the addition of a few drops of hydrochloric acid if necessary; and the iron was determined by precipitation with ammonium hydroxide, drying the precipitate, igniting, and weighing as ferric oxide, Fe_2O_3.

On testing the aqueous solution of the residue containing the zirconium with potassium thiocyanate solution, not a trace of iron was discovered, showing that the separation had been a complete and successful one.

Several analyses were made, using varying relative amounts of the zirconium and iron salts.

I. 0·1824 grm. ferric chloride with 0·1262 grm. zirconium tetrachloride gave:—

0·0540 grm. ferric oxide = 29·50 per cent ferric oxide.
0·0615 grm. zirconium dioxide = 48·89 per cent zirconium dioxide.

II. 0·1763 grm. ferric chloride with 0·1890 grm. zirconium tetrachloride gave:—

0·0524 grm. ferric oxide = 29·55 per cent ferric oxide.
0·0920 grm. zirconium dioxide = 48·83 per cent zirconium dioxide.

III. 0·3064 grm. ferric chloride with 0·1620 grm. zirconium tetrachloride gave:—

0·0910 grm. ferric oxide = 29·60 per cent ferric oxide.
0·0788 grm. zirconium dioxide = 48·79 per cent zirconium dioxide.

IV. 0·6564 grm. ferric chloride with 0·2544 grm. zirconium tetrachloride gave:—

0·1931 grm. ferric oxide = 29·36 per cent ferric oxide.
0·1240 grm. zirconium dioxide = 48·78 per cent zirconium dioxide.

V. 0·1276 grm. ferric chloride with 0·6924 grm. zirconium tetrachloride gave:—

0·0390 grm. ferric oxide = 29·70 per cent ferric oxide.
0·3385 grm. zirconium dioxide = 49·04 per cent zirconium dioxide.

On analysing the ferric chloride used it gave 29·44 per cent ferric oxide, while the zirconium chloride gave 48·97 per cent zirconium dioxide. The latter salt also showed a contamination by iron equivalent to 0·16 per cent ferric oxide, and in the percentages given in the above analyses, an allowance is made for this correction.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·50	29·55	29·60	29·36	29·70
Zirconium dioxide..	48·97	48·89	48·83	48·79	48·78	49·04

In making a practical use of this separation it is only necessary to obtain the two metals in solution in the form of chlorides and then the details as already given may be applied.

On the Delicacy of the Separation of Iron from Zirconium.

The fact that zirconium oxychloride is perfectly white in colour should not be taken as a final indication that it is absolutely free from traces of iron; and this should be borne in mind in the preparation of salts for atomic weight determinations. In order to establish the accuracy of the method which has been described for the separation of iron from zirconium, a series of delicate experiments was carried out with the object of determining approximately the quantity, if any, of iron still remaining with the zirconium salt.

Zirconium tetrachloride, contaminated with iron, was treated with a little water in order to convert it into the oxchloride; it was then digested with ether, and a drop of hydrochloric acid added. The ether was filtered off and the perfectly white residue of zirconium oxychloride was washed several times with absolute ether to ensure the removal of the last traces of the iron salt.

A solution of ferric chloride was made, one c.c. of which contained 0·0000001 grm. ferric chloride. This was called solution No. 1.

Another solution of ferric chloride was made, one c.c. of which contained 0·00000005 grm. ferric chloride. This was called solution No. 2.

One c.c. of solution No. 1 was placed in a test-tube, and to this were adeed one c.c. of hydrochloric acid (sp. gr. 1·17), and one c.c. of a solution of 10 grms. ammonium thiocyanate in 100 c.c. of water, and the volume of the liquid was made up to 10 c.c. A slight pink colour was noticed. One c.c. of solution No. 2 was treated in the same manner, and a just perceptible pink tinge was observed.

One-tenth grm. of zirconium tetrachloride was dissolved in 5 c.c. of water, and treated as above; a dark red colour immediately appeared.

One-tenth grm. of the zirconium oxychloride as freed from iron was dissolved in 5 c.c. of water, and treated in a similar manner; a very slight pink tinge was perceptible. On comparing this with solutions No. 1 and No. 2, it was found that the intensity of colouration of the zirconium oxychloride solution was between that of the two iron solutions. From this it is to be concluded that the ratio between the amount of iron salt and that of the zirconium salt present in the zirconium oxychloride is approximately between the limits of 1 : 200,000 and 1 : 100,000.

The tetrachloride of zirconium, before its separation from iron, showed a percentage of the latter equivalent to about 0·16 per cent ferric oxide. By the above comparison this percentage appears to be reduced to something approximately between the limits of 0·001 and 0·0005 per cent. The solution of hydrochloric acid used in these experiments was purified to such an extent that 1 c.c., when treated with 1 c.c. of the ammonium thiocyanate solution, on dilution to 10 c.c. gave no perceptible pink colouration.

The observations of those delicate tints were made immediately after mixing the solutions, and by comparison with an equal volume of distilled water. On standing for a time the colours were apparently discharged.

(To be continued).

THE ESTIMATION OF BORIC ACID.*

By F. A. GOOCH AND LOUIS CLEVELAND JONES.

The estimation of boric acid by treating the salts of that acid with sulphuric acid, distilling with methyl alcohol, evaporating the distillate over magnesium oxide, igniting and weighing, was proposed by Rosenbladt (*Zeitschr. für Anal. Chem.*, xxvi., 21). A little later, and without knowledge of Rosenbladt's experience, a somewhat similar process (*Am. Chem. Journ.*, ix., 23), which consisted in the treating of the compound of boric acid with acetic acid or nitric acid, distillation with methyl alcohol, evaporation of the distillate over calcium oxide, and ignition of the residue, was described by one of us. In the course of the development of this process, it transpired that the insolubility of magnesium oxide retards the absorption of boric acid by that substance, and that the more soluble calcium oxide retains boric acid more actively and is therefore to be preferred.

Points in the treatment upon which special emphasis was laid in the original description of this process were the choice of a suitable apparatus for the distillation, the employment of a loosely stoppered receiver for the reception of the distillate upon slaked lime, the careful removal of water from the substance in the retort before acidifying and treating with the methyl alcohol, regulated use of acid, and care in the evaporation and ignition.

The attainment of good results in this process depends upon attention to details. Modifications have been suggested by several investigators. Thus, instead of igniting the calcium oxide in a large platinum crucible, transferring it to the receiver to hold the boric acid, and returning the calcium oxide with the distillate to the same crucible for subsequent ignition of the residue, as was originally proposed, Penfield (*Am. Journ. Sci.*, xxxiv., 222), prefers to ignite the calcium oxide in a small crucible, to collect the distillate in ammoniacal water, to evaporate the latter over the calcium oxide in a large platinum dish, and to transfer this residue back to the small crucible for the final evaporation and ignition. Kraut (*Zeitschr. für Anal. Chem.*, xxxvi, 3), suggests a modification of form in the apparatus with no other essential change in conditions. Moissan (*Comptes Rendus*, cxvi., 1084), has suggested changes in the apparatus and avoids a transfer of the calcium oxide—collecting the distillate by itself in a closed receiver, trapped with an ammonia bulb to prevent the escape of the boric acid from the distillate. Furthermore, Moissan's process calls for the use of an amount of calcium oxide from fifteen to twenty times greater than that theoretically required. From our experience it seems obvious that the demand for this amount of calcium oxide arises from an excessive use of nitric acid in the retort and the consequent modification of conditions in the distillate. Fortunately this difficulty may be avoided by the use of a little phenolphthalein as an indicator in the retort and care to limit the addition of nitric acid to the amount required to produce distinct acidity. The addition of a drop of the acid and another of the indicator should be repeated once or twice during the distillation to insure the replacement of the acid volatilised from the salt slightly decomposed in the process. The effect of much nitric acid is bad, not only because it neutralises the calcium oxide when it passes to the distillate, but because when it is used a tendency is developed on the part of the dried mixture of calcium hydroxide and borate to puff explosively if this ignition is begun as soon as the residue is dry. If the residue is heated gradually and as strongly as possible over a radiator before the flame is actually applied to the crucible, no such action takes place; we are disposed to attribute it to the effect of the nitrate and nitrite, produced by the absorption of nitrous fumes in the lime, upon the alcohol or other organic matter retained by the lime in the evaporation and drying unless the latter process is prolonged at high temperature.

That good results may be obtained with small amounts of calcium oxide provided care as to the use of nitric acid and the conditions of ignition be taken, is shown by the figures of the original description and by the following experiments, in which phenolphthalein was employed as an indicator and the residue heated strongly over the radiator before actual ignition.

CaO taken. Grm.	B_2O_3 taken. Grm.	B_2O_3 found. Grm.	Error. Grm.
2·3405	0·1788	0·1792	+0·0004
1·7620	0·1790	0·1785	—0·0005
2·1757	0·1824	0·1840	+0·0016
2·5656	0·1788	0·1786	—0·0002

These results are accurate within reasonable limits. On the other hand, without care to ignite gradually we have noted errors of from 0·0030 grm. to 0·0060 grm. in the process otherwise conducted similarly. Doubtless the use of large amounts of calcium oxide as suggested by Moissan may serve the purpose of diffusing the explosive mixture through a mass of inert matter sufficient to pre

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vii, 1899,

vent violent puffing, but care to heat over the radiator as strongly as possible before opening the flame directly to the crucible answers the same end. The difficulty does not exist when acetic acid is used in place of nitric acid, though even in this case it is safer to use the radiator in the first stages of heating, thus avoiding the danger of mechanical loss by too rapid ignition.

Following are determinations made by this method with the use of acetic acid :—

CaO taken. Grm.	B_2O_3 taken. Grm.	B_2O_3 found. Grm.	Error. Grm.
0·9977	0·2065	0·2062	−0·0003
1·0220	0·2067	0·2070	+0·0003
1·3717	0·2077	0·2075	−0·0002
1·1310	0·1791	0·1795	+0·0004

The results of the preceding table, as well as those of the investigators mentioned, are a sufficient answer to the criticism of Reischle (*Zeitschr. fur Anal. Chem.*, xxvi., 512), that acetic acid and nitric acid do not liberate boric acid in the distillation process so that good results may be obtained. Moreover, it has been shown by one of us (Jones, *Amer. Journ. Sci.*, v., 442) that even carbonic acid is strong enough to bring about complete volatility of boric acid with methyl alcohol.

The Use of Calcium Oxide as a Retainer.

Quite recently Thaddeeff (*Zeitsch. fur Anal. Chem.*, xxxvi., 568) has advocated the abandonment of calcium oxide as an agent for holding boric acid in the evaporation of alcoholic and aqueous solutions, on account of the hygroscopic nature of the oxide and the consequent difficulty of securing it in definite conditions for weighing, and proposes, instead of using calcium oxide, to retain and estimate boric acid in solution by converting it into the form of potassium borofluoride.

In the final modification of Thaddeeff's method the proposal is made to liberate the boric acid from its compounds by sulphuric acid, to volatilise it in methyl alcohol with the aid of a current of dry air, to catch the distillate in potassium hydroxide, to treat the mixture of hydroxide and borate with hydrofluoric acid in excess and evaporate in the steam bath, to digest the residue of fluoride and borofluoride at normal temperatures for two hours with 50 c.m.³ of a potassium acetate solution (sp. gr. 1·14), and for twelve hours more after adding 100 c.m.³ of ethyl alcohol (sp. gr. 0·805), to filter on paper, wash the residue with 62 to 72 c.m.³ of alcohol (sp. gr. 0·805°), dry at 100° and weigh as potassium borofluoride, after which the borofluoride is to be dissolved in boiling water and tested with calcium chloride for possible contamination by the presence of a fluoride. Plainly Thaddeeff's procedure presents at the outset difficulties; for besides the inconvenience of conducting long digestions with reagents of regulated strength, the difficulty of procuring hydrofluoric acid free from silica, which if present (as it usually is, in the so-called chemically pure hydrofluoric acid of commerce) would be retained in the borofluoride as potassium fluosilicate, the inaccuracy of the dried paper filter, and the obvious uncertainty of success in an attempt to wash a mixture of acid potassium fluoride and potassium borofluoride in potassium acetate and alcohol, so that the one shall be rendered entirely soluble while the other remains sensibly unaffected; besides these objections, there is the theoretical probability that boric acid must be lost by volatilisation during the evaporation of the solution of the mixed salts in the presence of free hydrofluoric acid. This last point was put to the proof by submitting to distillation in a platinum retort a mixture of equal quantities of borax and potassium hydroxide with an excess of hydrofluoric acid, collecting the distillate in potassium hydroxide, evaporating it to dryness, and testing it for the presence of boric acid. When this residue from the evaporated distillate was treated with sulphuric acid and methyl alcohol, the burning alcohol vapour gave plainly the green flame of boric acid. Another portion showed clearly the presence of boric acid when acidulated with hydrochloric acid tested with turmeric paper. No boric acid could be detected in any of the reagents used. It is plain, therefore, that boric acid does volatilise upon the evaporation of a mixture of potassium fluoride and borofluoride in acid solution. The amount of such loss is disclosed in the record of the following experiment. Portions of a standard solution of boric acid, prepared by dissolving a known weight of anhydrous boric oxide in a litre of water, were mixed with a solution of potassium hydroxide (free from silica and standardised by conversion to the chloride) in the proportions to form the potassium borofluoride, and an excess of hydrofluoric acid was added. The mixture was evaporated and the residue was dried and weighed at 100°, the whole operation being conducted in platinum.

HKF_2 equivalent to KOH taken. Grm.	B_2O_3 taken. Grm.	$KFBF_2$ theoretical weight Grm.	$KFBF_2$ found. Grm.	Error in terms of $KFBF_2$. Grm.	Error in terms of B_2O_3. Grm.
0·3531	0·1582	0·5701	0·5580	−0·0121	−0·0033
0·3192	0·1430	0·5154	0·5100	−0·0054	−0·0015
0·3192	0·1430	0·5154	0·5030	−0·0124	−0·0034
0·3192	0·1430	0·5154	0·5088	−0·0066	−0·0018
0·3192	0·1430	0·5154	0·5114	−0·0040	−0·0011

In Experiments 1 to 3 the volume of the solution evaporated was about 50 c.m.³. In Experiment 4 this volume was reduced about one-half before acidifying with hydrofluoric acid, while in Experiment 5 the solution was diluted about one-half before adding the hydrofluoric acid. It is plain, therefore, that in this single step of Thaddeeff's process there is a considerable error of deficiency. On the other hand, the errors for the full process as laid down by Thaddeeff have been in our experience invariably differences of excess—presumably because the loss due to volatilisation of boric acid has been overbalanced by the inaccuracy in washing. It is plain that the process can give true indications only by the balancing of considerable errors.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 16th, 1899.

Professor Dewar, F.R.S., President, in the Chair.

Mr. W. S. Crouch was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George Smith Bratby, Oak Field, Hale, Bowdon, Cheshire; John Elias Hughes, Birchville, Wrexham; Lauder William Jones, University of Chicago, Chicago, Ill., U.S.A.; Frederick William Pittuck, 19, Stratford Grove, Newcastle-on-Tyne; Harold McLean Read, 127, Warwick Road, Earl's Court, S.W., Harry Alexander Thiersch, 8, Clifton Gardens, W.; Arthur Luvian Wade, 28, West Kensington Gardens, W.; Charles Walker, Scott Chambers, Pitt Street, Sydney, N.S.W.; Fred Sheasby Watson, Springside, Disley, Cheshire.

A ballot for the election of Fellows was held, and the following subsequently declared duly elected :—

Samuel William Allworthy, M.A.; John Frank Blackshaw; Stuart Blofeld, B.A., B.Sc.; Robert Alfred Bolam, M.D.; Bertram H. Bowles; William H. Branscombe, B.A.; H. Cort H. Carpenter, B.A., Ph.D.; Thomas John Cheater; Frank Cope; Thomas James Cozens; James Washington Epps; Harry Estcourt Estcourt; Ernest

Barratt Fairweather; George Cecil Fry, B.Sc.; Colin Charlwood Frye; Edmund Vivian Gabriel, M.A.; John Golding; Samuel Godfrey Hall; Henry Winston Harper, M.D.; Harold Brewer Hartley, B.A.; George Ward Hedley, M.A.; James Hembrough; Thomas Anderson Henry; Harold Octavius Knight; Edward Flatman Linstead; Alfred Lucas; Thomas Luxton, B.A., B.Sc.; Thomas Mackenzie; Samuel Montagu Martin; Joshua Maudsley, B.A.; James McCracken; Arthur Mirrlees, B.A.; Bernhard Mohr, Ph.D.; John Cavendish Molson; John Trengrove Nance, B.A.; William Walter Scott Nicholls; Dudley Northall-Laurie; John O'Sullivan; James Henry Pizey; Robert Coleman Price; Horace Seymour Pyne; James Roberts, Jun.; Frederick William Skirrow, B.Sc.; Frederick Soddy, B.A.; Arnold Stevenson, B.A.; Charles Emerique Szarvasy, Ph.D.; Louis Heathcote Walter, B.A.; Arthur Lee White, B.Sc.; Henry Fox White; William Arthur Williams; Thomas Wilson Wormell, B.Sc.

The President announced that Mr. C. E. Groves, F.R.S., had resigned the Editorship of the Society's *Journal*, and that Dr. W. P. Wynne, F.R.S., had been appointed to succeed him. The Council had recorded their sense of Mr. Groves's services to the Society in a vote of thanks, a copy of which would be engrossed on vellum and presented to him at the Anniversary Meeting.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As *President*—Professor T. E. Thorpe, Ph.D., D.Sc., LL.D., F.R.S., *vice* Professor James Dewar, M.A., LL.D., F.R.S.

As *Vice-Presidents*—Mr. C. E. Groves, F.R.S., and Professor Thomas Purdie, Ph.D., F.R.S., *vice* Professor F. R. Japp, M.A., LL.D., F.R.S., and Professor W. A. Tilden, D.Sc., F.R.S.

As *Hon. Secretary*—Dr. Alexander Scott, F.R.S., *vice* Dr. W. P. Wynne, F.R.S.

As *Hon. Treasurer*—Professor W. A. Tilden, D.Sc., F.R.S., *vice* Professor T. E. Thorpe, LL.D., F.R.S.

As *Ordinary Members of Council*—Mr. H. Brereton Baker, M.A., Professor F. Clowes, D.Sc., Dr. G. T. Moody, and Professor James Walker, D.Sc., *vice* Professor Bedson, D.Sc. Mr. Hehner, Professor McLeod, F.R.S., and Dr. Scott, F.R.S.

Dr. H. T. Brown, F.R.S., Dr. A. W. Crossley, and Mr. R. J. Friswell were appointed to audit the Society's accounts.

Of the following papers those marked * were read:—

*26. "*On the Absorption Spectrum and Constitution attributed to Cyanuric Acid.*" By W. N. Hartley, F.R.S.

The spectrum of cyanuric acid was described by the author in 1882 (*Trans.*, xli., 84), as exhibiting an absorption band between wave-lengths 2747 and 2572, and the formula deduced was that of a symmetrical trihydroxybenzene in which the three CH-groups are replaced by three nitrogen atoms. The bulk of the original preparation having been carefully preserved, its absorption spectrum has been photographed again with the improvements and modifications devised by the author in 1883 (*Phil. Trans.*, 1885, clxxvi., 471). The results show that 2·5 grms. of cyanuric acid, when dissolved in hot distilled water, made up to 500 c.c. and placed in cells respectively 200 m.m. and 100 m.m. in length, exhibited nothing which could be described as an absorption band. In the first case the warm solution cut off the spectrum sharply at about wave-length 2572, but transmitted the rays only weakly from about 3330, and in the 100 m.m. cell the spectrum was cut off sharply at 2483. The spectra thus obtained are in complete harmony with the formula $(H{\cdot}N{:}C{:}O)_3$, but not with that formerly given.

A searching examination of all the conditions and circumstances surrounding the preparation of the solutions and photographs of the original spectra shows that the possibility of any foreign substance getting into the cyanuric acid was almost precluded. But as the specimen was purchased there might have been, perhaps, a m.grm. or less of some solid substance adhering accidentally to the lip of the bottle, or attached to the cork, which would be weighed out with the first quantity of crystals. There are many well-known substances, of which a m.grm. would suffice to produce the effect observed.

*27. "*A Study of the Absorption Spectra of Isatin, Carbostyril, and their Alkyl Derivatives in relation to Tautomerism.*" By W. N. Hartley, F.R.S., and James J. Dobbie, D.Sc., M.A.

In this paper the authors trace the relation between the curves of molecular absorption and the constitution of isatin, carbostyril, and their alkyl derivatives. They start from the fact (*Phil. Trans.*, 1879, clxx., Part I., 257) that the substitution of a methyl or ethyl group for an atom of hydrogen, without other alteration in the structure of the substance, merely increases the general absoption,—*i.e.*, slightly shortens the transmitted spectrum without making any difference in the character of the absorption, and show that when the curves of molecular absorption of the substances studied are compared, a very close resemblance is seen to exist between the parent substance and one of the two isomeric derivatives.

In the carbostyril group the spectra of carbostyril, methylcarbostyril, and methyl- and ethyl-pseudocarbostyril are compared. Carbostyril and methylpseudocarbostyril both show an absorption band in the same position, and the spectra of the two substances are, in other respects, almost identical, the only difference being that the general absorption is slightly increased in the case of methyl- and ethyl-pseudocarbostyril, which is the effect usually produced when alkyl radicles are substituted for hydrogen. The spectra of methylcarbostyril differ in a marked manner from those of carbostyril and methylpseudocarbostyril; the absorption band occupies a different position, is less persistent and less intense than the corresponding band of the latter, and the amount of the general absorption is less.

Isatin and its derivatives show similar relations. In the spectra of isatin there are two absorption bands. The spectra of methylpseudoisatin closely resemble those of isatin, likewise exhibiting two absorption bands, and about the same extent of general absorption. In methylisatin there is only one strong absorption band.

The authors conclude that the very close resemblance between the curves of molecular absorption of carbostyril and methyl- and ethylpseudocarbostyril and between those of isatin and methylpseudoisatin point to identity of constitution, and, inasmuch as the chemical behaviour of methylpseudocarbostyril and methylpseudoisatin show that these compounds are lactams, the lactam constitution must also be assigned to carbostyril and isatin. This conclusion agrees with that arrived at by Goldschmidt and Meissler (*Ber.*, 1890, xxiii., 253), who employed a purely chemical method in their investigations, and with the more recent results of Knorr (*Annalen*, 1896, ccxciii., 81).

A detailed account of the various spectra is given in the paper.

Discussion.

Dr. J. H. Gladstone said that the study of the selective absorption of the rays of light by different substances was a physical method of research which, in his opinion, had been too much neglected. It was capable, beyond doubt, of distinguishing between different compounds of an elementary substance, and, in some instances, of throwing light on their constitution. If the absorption of rays of light by a compound were always the sum of the absorption of its separate constituents, or if different compounds of the same element gave totally different spectra, this mode of analysis would be of little use: investigation showed, however, that similarity is often associated with suggestive differences. Thus, in the case of ferric

salts, the extreme red ray is always transmitted with the greatest ease, whilst the blue-green and other more refrangible rays are soon absorbed; yet the rapidity of absorption varies very much, as may be seen in the great difference in the degree of redness of such ferric salts as the nitrate and sulphocyanide. Observations such as these were much facilitated by placing the liquid in a hollow prism instead of in a cell with parallel sides, as, in this way, the gradual absorption of the various rays by different thicknesses could be seen and mapped at once. The absorption of different kinds of rays might be employed for the purpose of chemical research, each having, no doubt, its own story to tell, and fruitful results might be expected from the use, not only of the coloured rays of the visible spectrum and of the more refrangible rays which Professor Hartley is engaged in photographing, but also of the less refrangible heat rays, and even, perhaps, of the X rays in the future.

Professor Dobbie pointed out that the relation of such substances as isatin and its methyl derivatives to one another had long been a vexed question, and that it had not been found possible to solve it by means of chemical methods. The advantage of the spectroscopic method was that the uncertainty, due to possible shifting of the atoms in the course of a chemical reaction, did not arise. It was interesting to note that the results obtained by this method were in complete agreement with those most recently arrived at by chemical processes, in which care had been taken to eliminate, as far as possible, the sources of error inseparable from the older methods.

Dr. A. Harden referred to Schiff's work on the isolation of tautomeric forms of ethylic acetoacetate, and asked whether experiments had been made with the object of isolating and of examining spectroscopically the enolic form of isatin.

The President said that every physical method which in any way could aid in establishing the identity of a material under investigation was of the utmost importance to future workers. A substance might seem to be pure so far as evidence derived from ordinary analytical methods was concerned, and yet reveal the presence of impurity when its ultra-violet spectrum was examined. This was the case with water, the ultra-violet spectrum of which was most characteristic, and served to indicate the presence of water vapour in gases dried by the ordinary methods. He was inclined to think that some improvement might be made in the selection of the material for obtaining the ultra-violet spectrum. The cadmium spectrum was open to the objection that wide gaps existed in which no lines were present, and the use of a material such as iron, which gave a spectrum of lines more evenly distributed in the ultra-violet, would seem to be preferable.

Professor Hartley, in reply, said that, when working with rays of high refrangibility, it had been found best to use a quartz cell in which the faces were parallel.

The use of the iron spectrum for the study of absorption spectra had attracted his attention in the past, and was referred to in the paper published in 1879; the objections to its use were that too many lines were present, and that two very strong groups existed in the more refrangible part where absorption bands were likely to occur. The best electrodes for use were those made of cadmium-tin and cadmium-lead alloys containing 15 to 20 per cent of cadmium; the lines were sufficiently numerous and distinct, but not too strong, and there was, moreover, the continuous spectrum between them forming, as it were, a background.

The investigation of tautomeric compounds was in progress, and the results would form the subject of a separate communication to the Society.

*28. "*The Estimation of Nitrites and Nitrates by means of Ferrous Chloride.*" By A. Wynter Blyth.

The author has devised an apparatus in which nitrites and nitrates, either singly or together, can be estimated as nitric oxide by means of ferrous chloride. The essential feature of the apparatus is a mercury valve, which is made by connecting one end of a long delivery tube with the side tube of a flask, and causing the other to dip below the surface of mercury in the mercurial trough, the bend of the delivery tube being 770 m.m. above this level. The air from the flask is expelled by boiling, and a special feature is made of the ease with which successive vacua can be obtained in such a flask. The author has found that nitric oxide is evolved from nitrites at once, whereas there is an appreciable interval of from one to two minutes before any nitric oxide is formed from nitrates. Nitrates yield the whole of the nitric oxide only when the flask is evacuated several times. The results obtained with the apparatus are accurate.

Discussion.

Mr. J. H. Coste said that eight years ago he had used in the laboratory of the Royal Agricultural Society of England an apparatus similar in principle to that described by the author, but of simpler construction. It was, he believed, devised by Dr. Walter Leather, and was described in Addyman's "Agricultural Analysis." The indiarubber stopper of the evolution flask was provided with a water jacket, and fitted with a delivery tube considerably over 760 m.m. in length, dipping under the surface of mercury in a tray placed at a lower level. The use of the rising tube described by the author was thus obviated. The results obtained and the ease in manipulation left little to be desired.

Mr. Wynter Blyth, in reply, stated that he did not claim anything new in the principle of the apparatus; it had, indeed, been applied for some time in the construction of mercury pumps. He was glad to hear that the same kind of valve was in use successfully elsewhere.

*29. "*Estimation of Boric Acid Mainly by Physical Processes.*" By A. Wynter Blyth.

When a methylic alcohol solution of boric acid is distilled, 78 per cent of the acid collects in the first fifth of the distillate; a dilute aqueous solution, on the contrary, loses very little of the acid until concentration has taken place. These facts are applied to the detection of minute traces of boric acid in various substances.

It is shown that even small quantities of boric acid can be estimated by polarimetric methods. For this purpose, 3 grms. of dextrotartaric acid are dissolved in methylic alcohol, and the solution of boric acid in methylic alcohol added so as to make exactly 20 c.c. at 18°. The increase of rotation is then observed. For quantities amounting to 0·05—1·03 per cent, a 5 dm. tube is required The specific rotation, calculated on the constant amount of the tartaric acid present, is given for quantities ranging from 0·05—3 per cent.

When boric acid is boiled with a solution of sodium carbonate carbon dioxide is evolved, in accordance with the equation $Na_2CO_3+4H_3BO_3=Na_2B_4O_7+CO_2+6H_2O$, the proportion being 0·177 part by weight for every part of boric acid present. After boiling and concentrating, the solution is made up to a definite volume, and the conductivity at 18° measured by Kohlrausch's method. From the reduction of the resistance, the amount of boric acid, as sodium borate, can be estimated provided the sodium carbonate solution employed is always of the same strength. A table is given of the values of K (resistance of cell divided by resistance in ohms, of solution), and the results are plotted out as a curve. After the resistance has been determined, an aliquot part or the whole of the solution is transferred to a flask connected with the apparatus described in the preceding abstract, and the carbon dioxide estimated by treatment with an acid.

Discussion.

Mr. A. C. Chapman pointed out that small quantities of impurities in the boric acid would be likely to sensibly affect the accuracy of physical methods such as those suggested by the author, and asked how the whole of the boric acid could be obtained from such substances as

food products in a state of sufficient purity for the application of these methods.

Mr. Wynter Blyth, in reply, said that distillation with methylic alcohol gave the methyl compound in a state of sufficient purity for the purpose of estimation by the polarimetric method.

30. "*The Interaction of Ethylic Sodiomalonate and Mesityl Oxide. A Correction.*" By Arthur W. Crossley.

Since the publication of a preliminary notice on the action of ethylic sodiomalonate on mesityl oxide (*Proc.*, 1898, xiv., 247) Dr. Vorländer of Halle has pointed out to the author that the reaction has already been studied. The substance obtained by hydrolysis of the condensation product is dimethylhydroresorcine, $C_8H_{12}O_2$, and possesses half the molecular weight assigned to it by the author, and although having marked acid properties is not a carboxylic acid.

The author expresses his regret at not having known of Dr. Vorländer's work.

31. "*On Lössner's Benzoylethyloxysulphocarbamic Acid, and the Formation of Pseudoureas.*" By Augustus Edward Dixon, M.D.

Benzoyl chloride interacts with a hot saturated solution of potassium thiocyanate, yielding potassium chloride and a compound, $C_{10}H_{11}NSO_2$, regarded by Lössner (*Journ. Prakt. Chem.*, 1874, [ii.], x., 237) as benzoylethyloxysulphocarbamic acid, COPh·NEt·CO·SH. Miquel (*Ann. Chim. Phys.*, 1877, [v.], xi., 334), showed later that the same compound is produced from benzoylthiocarbimide and ethylic alcohol, and that consequently it is not an acid, but an "ether," COPh·NH·CS·OEt. With caustic potash, it affords a potassium derivative, from which by interaction with ethylic iodide, the corresponding ethylic compound is obtained; the latter is decomposed by ammonia into mercaptan, together with a supposed unsymmetrical benzoylethylurea, $COPhn·NEt·CO·NH_2$.

In the present paper, it is shown that the constitution assigned to this "urea" is not in accordance with its properties. On hydrolysis, it yields carbonic and benzoic acids, alcohol, and ammonia, but no ethylamine, from which it follows that the ethylic group is not attached to nitrogen, and the conclusion is drawn that the supposed urea of Lössner is really the ethylic salt of a benzoylated imidocarbamic acid, $COPh·N:C(OEt)·NH_2$. Corresponding compounds have now been obtained, which bear towards the ureas a relation similar to that subsisting between the pseudothioureas and the thiocarbamides: to maintain uniformity of nomenclature, it is proposed that such imido-derivatives of organic salts of carbamic acid should be termed pseudoureas generically.

The constitution attributed by Lössner to the ethylic derivative from which the above ethyl-ψ-*n*-benzoylurea is obtained is COPh·NEt·CO·SEt; its properties, however, are inconsistent with this structure, and the author assigns reasons for representing it by the formula COPh·N:C(OEt)·SEt. If the potassium compound from which the latter is produced be similarly constituted, Miquel's formula for Lössner's benzoylethyloxysulphocarbamic acid requires further modification into that of the tautomeric ethylic imidobenzoylthiocarbonate, COPh·N:C(OEt)·SH.

Methyl-ψ-n-benzoylurea, COPh·N:C(OMe)·NH_2, is deposited from light petroleum in fern-like masses of white, flattened crystals, melting, without decomposition, at 77—78°. When boiled with alkali, or heated with water at 150—160° under pressure, it is hydrolysed into carbonic and benzoic acids, ammonia, and methylic alcohol; no ethylamine could be detected. Its isomeride, *ab-benzoylmethylurea*, COPh·NH·CO·NHMe, is prepared by desulphurising the corresponding thiocarbamide with silver nitrate; the thiocarbamide separates from alcohol in tufts of shining needles, the urea in colourless, thick prisms; they melt at 152° and 171° respectively.

Ethyl-ψ-n-benzoylurea, COPh·N:C(OEt)·NH_2, forms rhombohedral crystals melting at 74—75° without decomposition. Its isomeride, *ab*-benzoylethylurea, is stated by Miquel to melt at 192°, or, according to Leuckhart (*Journ. Prakt. Chem.*, 1880, [ii.], xxi., 33), at 168°. When prepared from the thiocarbimide (m. p. 130—131°) by means either of silver nitrate or, as described by Miquel, of yellow oxide of mercury, it was found to melt at 114—115°.

Anisoilthiocarbimide, $OMe·C_6H_4·CO·NCS$, is obtained, in solution, by heating the corresponding chloride, $OMe·C_6H_4·COCl$, dissolved in benzene, with lead thiocyanate. It unites with alcohol, forming *anisoilthiourethane* or, *ethylic imidoanisoilthiocarbonate*,

$$OMe·C_6H_4·CO·N:C(SH)·OEt,$$

which crystallises in small, white needles melting at 70—71°. The *potassium derivative* of the latter melts at about 222° (uncorr.); when boiled in alcoholic solution with ethylic iodide, and then saturated with ammonia, it yields *ethyl-ψ-n-anisoilurea*, $OMe·C_6H_4·CO·N:C(OEt)·NH_2$, in white, transparent prisms melting at 69—70°.

Anisoilthiocarbimide unites spontaneously with nitrogenous bases forming thioureas and thiocarbamides; the following are described. *Anisoilthiourea*, $CSN_2H_3·C_8H_7O_2$, forms rhombs and octahedra melting at 216—217°. By fusion with chloracetic acid, it yields *anisoilthiohydantoin* [*n*-anisoilthiourantoin (*Trans.*, 1897, lxxi., 638)], a pale-yellow solid, nearly insoluble in the ordinary solvents, and decomposing between 222° and 230°. *ab-Anisoilphenylthiocarbamide* crystallises from alcohol in brilliant prisms melting at 126°; the corresponding *ortho-* and *para-tolyl* compounds melt at 126·5° and 127—128° respectively. *ab-Anisoilmethylthiocarbamide* melts at 143—144°; the *ethylic* homologue melts at 126·5—127·5°, and yields, on desulphurisation, the symmetrical urea, $C_8H_7O_2·NH·CO·NHEt$, isomeric with the above ψ-compound; it melts at 146—147°. *ab-Anisoilbenzylthiocarbamide* forms colourless prisms melting at 127—128°. *n-Anisoil-ν-phenylbenzylthiourea*, $C_8H_7O_2·N:C(SH)·NPnBz$, from the thiocarbimide and benzylaniline, occurs in brillant rhombic plates melting at 142—143°. It not desulphurised by boiling with alkaline solution of lead, in which respect it differs from the other anisoil thio-compounds described.

32. "*On Certain Isomeric Tertiary Benzylthioureas.*" By Augustus Edward Dixon, M.D.

n-Phenyl-ν-methylbenzylthiourea,—

$$NPh:C(SH)·NMe·CH_2Ph,$$

was obtained, in quantitative amount, from phenylthiocarbimide and methylbenzylamine; it formed long, brilliant, silvery prisms melting at 129—130°. Its isomerides, NMe:C(SH)·NPhBz, and NBz:C(SH)·NMePh, melt at 121° and 85° respectively. By desulphurisation with silver nitrate, it afforded the *urea*, NHPh·CO·NMeBz, which crystallised in thin, pearly needles, melting at 134—135°.

n-Benzyl-ν-methylbenzylthiourea, NBz:C(SH)·NMeBz, prepared from benzylthiocarbimide and methylbenzylamine occurred in vitreous needles melting at 73°. Its isomeride, *n-methyl-ν-dibenzylthiourea*, NMe:C(SH)·NBz_2, formed white, rhombic crystals melting at 110—111°.

n-Methyl-ν-methylbenzylthiourea, NMe:C(SH)·NMeBz, formed vitreous, flattened crystals melting at 87·5—88·5°. Its isomeride, *n-benzyl-ν-dimethylthiourea*, NBz:C(SH)·NMe_2, crystallised in vitreous prisms melting at 98·5—99·5°.

These thioureas are practically insoluble in water; they are unaffected by boiling with alkaline lead tartrate, but are readily desulphurised by warming with nitrate of silver. It was remarked in 1893 (*Trans.*, lxiii., 540) that amongst the then known phenylated isomeric tertiary thioureas, the member containing the NPh-group had the highest melting-point; it is now shown that, in the methylphenylbenzyl series, this is also the case.

33. "*Is Camphene Unsaturated.*" By J. E. Marsh.

The more recent formulæ for camphor, such as that of Bredt, represent camphene, the typical hydrocarbon of

the group, as an unsaturated compound with one double linking. The reactions which appear to support this view are, firstly, the conversion of camphene into camphene glycol, $C_{10}H_{16}(OH)_2$, by the action of potassium permanganate (Wagner, *Ber.*, 1890, xxiii., 2307), and, secondly, the production of camphene dibromide, $C_{10}H_{16}Br_2$, by the action of bromine on camphene (Reychler, *Ber.*, 1896, xxix., 900). These reactions would be sufficient to establish the unsaturated character of camphene if it were a matter quite free from doubt that camphene glycol and camphene dibromide are the simple additive compounds they appear at first sight to be. The so-called camphene glycol, however, appears to possess none of the properties of a true glycol; and, in particular, the fact that it readily loses water, forming a compound having all the properties of an aldehyde, seems to be inconsistent with the view that it is a glycol at all. Moreover, the action of permanganate on camphene is much slower than is usually the case with an unsaturated compound. With regard to camphene dibromide, experiments have been made by the author which lead him to believe that this compound is not formed by the direct union of bromine and camphene, but is really the product of the interaction of bromine and camphene hydrobromide. By saturating camphene dissolved in glacial acetic acid with hydrogen bromide, and then adding bromine to the product, the so-called camphene dibromide is obtained in amount equal to about 70 per cent of the theoretical yield, whereas Reychler, by the direct action of bromine on camphene, obtained only 8 grms. from 27·7 grms. of camphene, which represents a yield of about 13 per cent. The chief product of the action of bromine on camphor is the substituted derivative bromocamphene, $C_{10}H_{15}Br$. In this reaction, then, it appears that bromine first replaces hydrogen in camphene, forming bromocamphene and hydrogen bromide; the hydrogen bromide is partly given off in the gaseous form, but in part also combines with the excess of camphene, forming camphene hydrobromide, which is then further acted on by bromine, giving the so-called camphene dibromide by the substitution of bromine for hydrogen. This reaction, therefore, cannot be brought forward as evidence in favour of the unsaturated character of camphene. It may be argued, perhaps, that the direct union of camphene with hydrogen bromide is in itself sufficient evidence of its unsaturated character. It does not, however, appear to be consistent with the nature of the double linking that it should resist the action of bromine and succumb to that of hydrogen bromide. Such a property is far more characteristic of the trimethylene ring, as Professor Perkin has shown, and may be characteristic also of other ring formations.

34. "*Formation of α-Pyrone Compounds and their Transformation into Pyridine Derivatives.*" By SIEGFRIED RUHEMANN.

The substances formed from α-pyrone derivatives by the addition of two molecular proportions of ammonia (*Proc.*, 1899, xv., 6), have been transformed into pyridine compounds. The view already expressed, that these additive products may be regarded as ammonium salts of unsaturated amino-acids, readily explains such a change. The transformation is effected by preparing from the ammonium salts the corresponding ethylic salts, which, on distillation, lose alcohol and condense to the pyridine compounds represented by the formulæ:—

$$CO_2Et.C\leqslant\begin{matrix}CPh{:}CH\\CMe\cdot N\end{matrix}\geqslant C\cdot OH,$$

I. M.-p. 184°.

$$CO_2Et\cdot C\leqslant\begin{matrix}CPh{:}CH\\CPh\cdot N\end{matrix}\geqslant C\cdot OH.$$

II. M.-p. 210°.

From the ethylic salt represented by formula I., the corresponding acid was prepared; this loses carbon dioxide at 240°, forming phenylmethylpyridone (m. p. 207—208°).

β-Diketones, like ethylic salts of β-ketonic acids, condense with ethylic phenylpropiolate under the influence of sodium ethoxide, forming α-pyrone derivatives of the general formula—

$$CPh\leqslant\begin{matrix}CH\text{——}CO\\C(COR){:}CR'\end{matrix}\geqslant O,$$

in which R and R' denote hydrocarbon radicles. Thus, from acetyl-acetone and from benzoylacetone, compounds have been obtained which melt respectively at 128° and 143—144°, and behave like α-pyrone derivatives with alcoholic ammonia.

Anniversary Meeting.

The Anniversary Meeting will be held on Wednesday, March 29th, at 3 o'clock in the afternoon.

CORRESPONDENCE.

THE ESTIMATION OF MANGANESE BY MEANS OF POTASSIUM PERMANGANATE.

To the Editor of the Chemical News.

SIR,—In my letter of February 3rd (CHEMICAL NEWS, vol. lxxix., p. 58), I intended to intimate that the low results obtained when estimating manganese by an iron standardised solution of potassium permanganate were not due to carbon either in the case of the method described by Mr. Brearley (CHEMICAL NEWS, vol. lxxv., p. 15), or in that recently described by myself (CHEMICAL NEWS, vol. lxxix., p. 25), and that the oxides precipitated in Mr. Brearley's method are therefore also "deficient in oxygen." This, of course, is immaterial when the solution is standardised in the same manner as the subsequent titrations are performed.

In regard to the method to which Mr. Brearley considers Gooch and Austen have applied the "faint praise which damns," I wish to remark that the method is their own, *not mine*, and that when I drew attention to their work to show that the presence of burnt gases had not that fatal effect Mr. Brearley would like to show they have I did not intend to endorse their method of applying them.

I am quite aware of the work done by Pickering—in fact, it would be difficult to miss these oft quoted figures; but I cannot say I have found the oxide variable when working under the conditions I describe. As an instance out of many, I give four estimations of manganese made recently on the same ferro by two operators working with platinum crucibles of varying size and thickness. The figures obtained were:—

1	80·78 per cent Mn
2	80·78 ,,
3	80·72 ,,
4	80·74 ,,

This cannot be said of ignition in a muffle unless it is very hot, and with the muffles in this laboratory it often happens they are not hot enough to make an accurate ignition of Mn_3O_4. This must happen in many instances where muffle furnaces are coke fired.

The following estimations of manganese in the same ferro will show the effect of temperature:—

5. The precipitate was heated in a muffle at bright red heat (say about 850° C.) for fifteen minutes, giving—

Mn .. .. 82·22 per cent.

The same precipitate was then heated over the blowpipe for three minutes, with the result that the figure obtained was the same as in the above four estimations, viz.—

Mn .. .. 80·78 per cent.

6. Another precipitate was heated in a muffle at red heat for two hours, which gave a result—

Mn .. .. 84·02 per cent,

The precipitate was then heated over the blowpipe for five minutes, giving—

Mn .. .. 80·74 per cent.

Two estimations were then made in a muffle at white heat (silver melted easily).

7. The precipitate was heated in a white-hot muffle for thirty minutes.—

Mn .. .. 80·88 per cent.

It was then heated over the blowpipe, the weight remaining constant—

Mn .. .. 80·88 per cent.

8. Another precipitate was heated in a muffle at white heat for thirty minutes, and gave—

Mn .. .. 80·78 per cent.

When heated over the blowpipe the result was the same—

Mn .. .. 80·78 per cent.

An estimation was then made by heating a precipitate over the blowpipe for a very much longer time than usual.

9. The precipitate was heated over blowpipe for five minutes—

Mn .. .. 81·02 per cent.

It was then heated fifteen minutes—

Mn .. .. 81·00 per cent.

And again fifteen minutes.—

Mn .. .. 81·00 per cent.

This estimation does not agree so well as the others, but it, however, shows that the continued action of the gases have no marked effect on the weight of the precipitate.

The impurities in all the above cases were removed as described in my recent article (CHEMICAL NEWS, lxxix., p. 25).

In the estimation of manganese as Mn_3O_4, it seems to me that the variability of the oxide is allowed to play too much the part of a "red herring," withdrawing attention from the very important fact that almost invariably impurities are present in the precipitate and must be removed. If these are ignored when working on 0·5 grm. of an 80 per cent ferro I have found an error of quite 1 per cent is sometimes introduced; silica is always present, derived presumably partly from the flask, and partly from the ferro; a black precipitate of iron, &c., with H_2S is also almost always present, and in the case of ores containing *lime* as much as 1·5 per cent will often be precipitated with the manganese. As an instance of how this error is usually ignored I may point out that Arnold ("Steel Works Analysis," p. 206), gives all due prominence to the possibility of the oxide varying, but mentions nothing about the probability of impurities being present.

In the method there described, however, precautions are certainly taken to prevent the presence of iron.

In conclusion, I am glad that Mr. Brearley allows that it is not impossible to obtain Mn_3O_4 in the manner I have described, and I presume I may infer that he will allow that if it is not impossible to do so once, it is not impossible to do so any number of times under the same conditions.—I am, &c.,

F. W. DAW.

Ebbw Vale, February 28, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 3, January 16, 1899.

Peroxidation of Cerium Dissolved in Alkaline Carbonates.—André Job.—Cerium dissolved in alkaline carbonates can exist in three states. (1) Cerous state, which corresponds to the oxide Ce_2O_3; (2) Ceric state, CeO_2; and (3) Perceric state, CeO_3. The author proves that the capacity of oxidation by air depends, in a great measure, on the nature of the salt which is dissolved in the alkaline carbonate. Thus, a solution of ammoniacal ceric nitrate remains in the ceric state in the air, without even the commencement of peroxidation, whilst a cerous solution of the nitrate passes at once into the ceric state, and then continues to fix the oxygen of the air, until a limit is reached which depends on the dilution.

The Source of Energy in Radio-active Bodies.—Sir William Crookes.—The author, referring to M. and Mdme. Curie's recent discovery of the new radio-active substances polonium and radium, states that the radiant activity of the new bodies needs neither the excitation of light nor the stimulus of electricity, but like uranium it draws its energy from some constantly regenerating and hitherto unsuspected store, exhaustless in amount. It can be conceived that uranium, polonium, and radium—bodies of densest atoms—have a structure that enables them to throw off the slow moving molecules of the atmosphere, while the quick moving molecules, smashing on to the surface, have their energy reduced, whilst the energy of the body is correspondingly increased. The energy thus gained seems to be employed partly in dissociating some of the molecules of the gas, and partly in originating an undulation through the ether, which, as it takes its rise in phenomena so disconnected as the impacts of the molecules of the air, must furnish a large contingent of light waves of short wave-length. The shortness in the case of these Becquerel rays appears to approach, without attaining the extreme shortness of ordinary Röntgen rays. The reduction of the speed of the quick moving molecules would cool the layer of air to which they belong, but this cooling would rapidly be compensated by radiation and conduction from the surrounding atmosphere; under ordinary circumstances, the difference of temperature would scarcely be perceptible, and the body would thus appear to perpetually emit rays of energy with no apparent means of restoration.

Triacetyl-morphine and Oxidation of Morphine.—H. Causse.—By the action of acid chlorides or anhydrides on morphine, $C_{17}H_{19}NO_3$, it has been shown that two of the oxygen atoms are in hydroxyl-groups—one phenolic, the other alcoholic. Attempts to prepare tri-substituted derivatives have so far been unsuccessful, and the author now demonstrates that the third oxygen atom of morphine is contained as carbonyl, CO, and that it is possible to obtain a triacetyl-derivative. The latter is a colourless crystalline body, insoluble in water, and giving no coloration with ferric chloride. Analysis ascribed to it the formula $C_{17}H_{17}N(C_2H_3O_2)_3.H_2O$. To confirm the presence of a CO group in morphine, oxidation was applied by means of iodic acid, the resulting CO_2 passed into baryta-water, and the barium carbonate separated and titrated. The CO_2 thus estimated corresponded to $C_{17}H_{19}NO_3 - CO_2$, or one molecule of carbonic acid for one molecule of morphine. Hence morphine may be written—

$$C_{16}H_{17}N\begin{matrix}OH\\OH.\\CO\end{matrix}$$

No. 4, January 23, 1899.

Properties of Aluminium.—A. Ditte.—In a former paper the author has shown that aluminium, though apparently unaltered by many chemical reagents, is in reality easily acted upon; this property not being apparent owing to a thin layer of alumina or gas being formed over the surface of the metal. He now continues his researches by examining whether the reactions are the same in the presence or absence of air, and shows that the alteration of the aluminium is distinctly facilitated by using atmospheres of oxygen and carbonic acid. The experiments are conducted with a mixture of sea-salt and acetic acid.

Researches on the Chemical State of some Elements contained in Siderurgical Products, Double Carbides of Iron, and other Metals.—Ad. Carnot and M. Goutal.—The authors show the existence of a certain number of well-defined carbides in siderurgical products. The following are the ones which have been isolated:—$3Fe_3C.Cr_3C_2$, $Fe_3C.3Cr_3C_2$, $Fe_3C.W.C$, $Fe_3C.Mo_2C$, $2Fe_3C.Mn_3C$, $Fe_3C.2Mn_3C$, $Fe_3C.4Mn_3C$.

Action of Oxidising Agents on certain Aromatic Compounds.—Œschner de Coninck and A. Combe.—The authors have further investigated the action of the chromic acid mixture on certain nitrogenous derivatives of the aromatic series with the object of discovering if there were no disengagement of nitrogen at the end of the reaction. In all cases they obtained only pure carbon dioxide—thus confirming their previous conclusions.

Action of Iodine Chloride on Monochlorbenzene in presence of Anhydrous Aluminium Chloride.—M. Friedel.—The author has investigated a new method of preparing chloriodine derivatives of the aromatic series. The method generally in use is that of digesting chloramines, and replacing the NH_2 groups by an atom of iodine. In the method here discussed, the chloro-derivatives themselves form the starting-point, and iodine is directly substituted for a hydrogen atom of the nucleus by means of boiling ClI. The reaction may be expressed as follows:—$C_6H_mCl_n + ClI = C_6H_{m-1}Cl_nI + HCl$, and takes place in presence of anhydrous aluminium chloride. A description of the preparation of para-iodo-chlorbenzene is given.

Biochemical Oxidation of Propylglycol.—André Kling.—Up to the present, no general method has existed of preparing glycols. After the publication of G. Bertrand's work on the oxidising action of the sorbose bacterium on polyvalent alcohols, André Kling applied the method to the case of glycols, and discovered oxidation to occur in a similar manner. The experimental substance was propyl glycol. This was treated with a culture of the sorbose bacterium for twenty days, after which the solution obtained was found to reduce Fehling's solution. The oxidation product was isolated by means of phenylhydrazin hydrochloride, being obtained as a yellow precipitate. The author intends to investigate the possibility of generalisation of this reaction.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., April 25, 1898.

The Salts of Pertungstic and Permolybdic Acids.—P. Melikoff and L. Pissarjewsky.—When the hypertungstates and hypermolybdates of K and Na are carefully heated with H_2O_2, mixed compounds of Na_2O_2, K_2O_2, and H_2O_2 are obtained. The authors have thus prepared and analysed the following compounds:—

$$Na_2O_2WO_4H_2O_2 + (Na_2O_2)^2WO_4 + 7H_2O,$$

$Na_2O_2WO_4H_2O_2$, $K_2O_4WO_3H_2O_2$, and $K_2O_2.MoO_3.H_2O_2$.

The Hypertitanates and Hyperborates.—P. Melikoff and L. Pissarjewsky.—The compound $NaOBO_3$ has not yet been obtained, but by adding an excess of H_2O_2 to a saturated solution of borax containing the equivalent quantity of NaHO, slightly soluble crystals are deposited in the form of monoclinic prisms; they are stable in the air, soluble in water at the ordinary temperature, and, by the action of dilute H_2SO_4, they give H_2O_2; their composition corresponds to the formula $NaBO_3 + 4H_2O$. By the action of H_2O_2 on the alkaline hypertitanates the two following crystalline compounds are obtained:—

$$(K_2O_4)_2TiO_3 + 10H_2O \text{ and } (Na_2O_2)_4Ti_2O_7 + 10H_2O.$$

The Condensation of Nitromethane with the Substituted Aromatic Aldehyds.—Th. Posner.—While the aldehyds of the fatty series react violently with nitromethane, the action of the aromatic aldehyds only takes place in the presence of condensation agents with the elimination of water. By heating 5 grms. of *o*-nitrobenzaldehyd up to 160° for eight or nine hours with 2 grms. of nitromethane and 0·5 grm. of chloride of zinc, the author obtained *o* nitrophenylnitroethylene (*ω-o*-dinitrostyrol); he also prepared di-*o*-nitrobenzylnitromethane $(NO_2.C_6H_4.CH_2)^2 + CH.NO_2$, by the action of chloride of *o*-nitrobenzyl on nitromethane soda.

Some Derivatives of Pyrocatechin.—Julius Hesse.—When di-soda pyrocatechin, suspended in alcohol, is heated for sixteen hours at 200° with dichloracetal, in a sealed tube, an oil is formed insoluble in the alkali, which is 1·2-phenylene-diethylorthoglyoxal,—

$$C_6H_4\begin{matrix}O\\O\end{matrix}>HC-CH<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}.$$

It is a volatile liquid with a density of 1·1252 at 14°, and boils at 150° with a pressure of 22 m.m.; concentrated H_2SO_4 colours it a reddish-violet.

A New Method for the Acetylation of the Amide Derivatives.—B. Pawlewski.—This method consists in making thioacetic acid react on the amide derivatives; the disengagement of SH_2 in this reaction, instead of H_2O as in the ordinary acetylation does not hinder the formation of the derived amide so much. The reaction is generally immediate, the products pure, and the return excellent—$RNH_2 + CH_3.CO.SH = R.NH.CO.CH_3 + H_2S$.

Action of the Primary, Secondary, and Tertiary Bases on Bromide of *o*-Xylylene.—A. Partheil and Th. Schumacher.—By causing bromide of *o*-xylylene to react on aniline the authors obtained dianilide of the *o*-xylylene, and with the *o*-toluidine the corresponding derivative; they also describe the derivatives of *p*-phenitidine and piperidine. They are unable to confirm Scholtz's observations that the tertiary amines cannot react on bromide of *o*-xylylene except with the formation of di-ammonium compounds.

Synthesis of 3 Oxyflavone.—T. Emilewicz and St. v. Kostanecki.—The authors used the ethoxyl derivative of *o*-oxybenzalacetophenone obtained by condensing benzaldehyd with resacetophenone, and then prepared 3-ethoxyflavone, $C_{15}H_9O_2(O_2H_5)$, which, by prolonged boiling with HI of density 1·7, was converted into 3-oxyflavone, $C_{15}H_2O_2(OH)$.

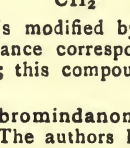
On α-Naphthoflavone.—St. v. Kostanecki.—2-aceto-1-naphthol condensed with benzaldehhyd gives 2-benzal-aceto-1-naphthol,—

$$C_{10}H_6\begin{matrix}OH\\CO\cdot CH=CH.C_6H_5\end{matrix},$$

of which the acetyl derivative transformed into dibromide gives, by the action of alcoholic potash, α-naphthoflavone,

$$C_{10}H_6\begin{matrix}O\,C.C_6H_5\\\|\\CO\,CH\end{matrix},$$ fusible at 154—156°.

Synthesis of the Flavone Derivatives.—W. Feuerstein and St. v. Kostanecki.—By the elimination of water from 2-oxybedzaldiacetophenone, the authors obtained a compound enclosing an oxygenated hexagonal nucleus.—

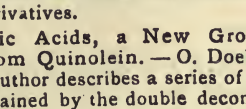


This compound is modified by boiling with mineral acids, and a substance corresponding to the formula $C_{23}H_{16}O_2$ is formed; this compound no longer contains the hydroxyl group.

The Oxybenzalbromindanones.—W. Klobski and St. v. Kostanecki.—The authors have examined the derived hydroxylised colouring-matters of benzalindanone, but as indanone itself was difficult to prepare they used one of its derivatives, 2-bromindanone. Bromindanone reacts very easily with benzaldehyd and gives 2-brombenzalindonone. The three isomerous monoxybenz-

aldehyds also condense with bromindanone in the presence of soda-lye. The authors describe several oxybrombenzalindanones thus obtained, as well as some of their derivatives.

Glauconic Acids, a New Group of Colouring-matters from Quinolein. — O. Doebner. — Under this name the author describes a series of acids of colouring-matters obtained by the double decomposition of aniline and its *p*-alcoyl derivatives with pyruvic acid and formaldehyd. Glauconic acid prepared by means of aniline is comparable to *p*-rosaniline, $HO.C\equiv(C_6H_4NH_2)_3$. It is a product of condensation of the carbinol group HO.C with 3 moleeules of dihydro-α-methyl-cinchonic acid,—



or an anhydride of this body.

MISCELLANEOUS.

The Chemical Laboratory at Wiesbaden. — The Chemical Laboratory Fresenius has during the Winter Term of 1898-99 been attended by forty-five students. Of these, thirty were from Germany, three from England, two respectively from Holland, Russia, and Brazil, and one from Austria, France, Norway, the United States of North America, the South African Republic, and India. Among those studying were several who were preparing for the Final Examination of Food Chemistry. There were three Assistants in the Instruction Laboratory, and twenty-four in the Experimental part (Examining Laboratories). No changes have taken place in the teaching staff of the Institution, to which, besides the Directors—namely, Herr Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, and Prof. Dr. E. Hintz—belong Herr Dr. med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and Architect J. Huber. The Summer Term begins on April 24th next. In this Winter Term, besides scientific work, there were many examinations carried on in the Experimental part (Examining Laboratories) in the interest of trade, industry, mining, farming, health, justice, and government.

MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Arts, 8 (Cantor Lectures). "Cycle Construction and Design," by Archibald Sharpe A.M.Inst.C.E.
—— Royal Institution, 5. General Monthly Meeting.
Tuesday, 7th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.
Wednesday, 8th.—Society of Arts, 8. "Cornish Mines and Miners," by J. H. Collins, F.G.S.
Thursday, 9th.—Society of Arts, 4.30. "Leprosy in India," by H. A. Acworth, C.I.E. (This Meeting will be held at the Imperial Institute).
—— Royal Institution, 3. "English Playhouses in the Sixteenth, Seventeenth, and Eighteenth Centuries," by Willian Poel.
Friday, 10th.—Physical, 5. "A Study of an Apparatus for the Determination of the Rate of Diffusion of Solids dissolved in Liquids" and "Note on the Source of Energy in Diffusive Convection," by Albert Griffiths, M.Sc. An Exhibition of Dr. A. Wehnelt's Electrolytic Current Interruptor for Ruhmkorff Coils, by A. A. Campbell Swinton.
—— Royal Institution, 9. "Measuring Extreme Temperatures," by Prof. H. L. Callendar, M.A., F.R.S.
Saturday, 11th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E, M.S.C.I.,
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Prof. W. FRESENIUS, Ph.D.
Prof. E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) — Prof. H. FRESENIUS, Ph.D.
Experimental Physics .. .. } Prof. W. FRESENIUS, Ph.D
Stöchiometry .. ..
Organic Chemistry .. .. } L. GRÜNHUT, Ph.D.
Chemical Technology .. ..
Microscopy, with exercises in Microscopic work .. .. } W. LENZ, Ph.D.
Chemistry and Analysis of Foods .. } Prof. H. FRESENIUS, Ph.D. Prof. W. FRESENIUS, Ph.D., and Prof. E. HINTZ, Ph.D.
Hygiene .. .. } Dr. med. G. FRANK.
Practical exercises in Bacteriology .. }
Technical Drawing, with exercises .. — J. HUBER.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. Kreidel's Verlag, at Wiesbaden, or to one of the Directors.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2050.

DEPOSITION OF BARIUM SULPHATE AS A CEMENTING MATERIAL OF SANDSTONE.*

By FRANK CLOWES, D.Sc.,
Emeritus Professor, University College, Nottingham.

Some years ago I described the occurrence of a peculiar sandstone over a large area in Bramcote and Stapleford, near Nottingham (*Roy. Soc. Proc.*, xlvi., 363). The sandstone was remarkable for its high specific gravity, and chemical analysis, supported by microscopical examination, proved that the high specific gravity was due to the existence in the sandstone of a large proportion of highly crystalline barium sulphate. In the rock itself the percentage of the sulphate varied from 33·3 to 50·1; and it evidently served as the binding or cementing material which held the sand grains together. The occurrence of this sandstone was stated by geologists to be unique in the United Kingdom.

Mr. J. J. H. Teall made an examination of a portion of the sandstone, and stated that, after breaking up a portion of the rock, he easily effected a separation of the sulphate from the sand by shaking the powder about in water: the small cleavage flakes thus obtained gave the optical characters of crystallised barium sulphate. Mr. Teall further stated that the barium sulphate occurred in large irregular crystalline patches, which included the sand grains; the sand grains, therefore, interrupted the reflections from the cleavage surfaces of the barium sulphate, giving rise to the appearance generally known as "lustre mottling" in petrographic literature.

I had noted this irregular distribution of the barium sulphate. In some parts of the rock the sulphate occurred in reticutated veins inclosing small patches of more or less loose sand grains; while in other parts of the rock the sulphate occurred in spherical or oval masses, between which looser sand was interspersed: occasionally, however, the barium sulphate was uniformly distributed.

The appearance presented by the weathered surface of the rock varied much according to the mode in which the resistant sulphate was distributed. When it was uniformly diistributed it formed an almost complete protection against weathering: this was seen on the cap of the great pillar of this rock, which is locally known as the "Hemlock Stone." The reticulated distribution of the sulphate caused the surface of the weathered rock to present a fretted surface, with the thin veins of sulphate projecting from the surface. When the sulphate had bound together spherical or oval masses in the substance of the sand, these were left in pebble-like forms as soon as the loose sand had been washed out from between them; and the resulting layers of loose sand, inclosing the rounded masses of sand bound together by the sulphate, had been not unnaturally classed by the geologists who had visited the district, as pebble-beds.

In discussing various ways in which this barium sulphate might have been deposited, I drew attention to the frequent deposition of barium sulphate from colliery water in the neighbourhood of Newcastle-upon-Tyne, and described some of these deposits (*Roy. Soc. Proc.*, June, 1889). And I further pointed out that Dr. Bedson had shown (*Journ. Soc. Chem. Ind.*, vi., 712) that barium chloride was a common constituent of the colliery waters in the district in which these barium sulphate deposits occur, and that it was present to the extent of 137·2 parts per 100,000 in some of these waters. It was evidently only necessary that water containing sulphuric acid or a soluble sulphate should mingle with the barium chloride water in order to explain the deposition of barium sulphate in the positions in which it was found. In colliery districts a frequent source of ferrous sulphate and of sulphuric acid is found in the iron pyrites in the beds of coal and shale. And I suggested that the constant occurrence of fine veins of calcium sulphate throughout the sandstone of the Nottingham district would account for a sulphate finding its way into the water which had been in contact with the rock. But in the Nottingham district all evidence of barium chloride in solution was wanting.

The occurrence of barium chloride in water from an artesian boring at Ilkeston has, however, recently been pointed out by Mr. John White, and he has described the nature of the strata through which the boring passed, and the results obtained by him in the chemical examination of the water, in *The Analyst* (February, 1899). The Ilkeston boring has been made in the immediate neighbourhood of the Brancote and Stapleford sandstone which contains the large proportion of barium sulphate. Since the barium chloride is found to the extent of 40·7 parts per 100,000 in the water from this boring, and seems to be a normal constituent of the water, it would appear that soluble barium salts are still abundant in the district, and may therefore have given rise to the deposition of the barium sulphate in the original sand beds. The crystallisation of the sulphate around the sand grains would then cause it to act as a compact insoluble cementing material.

It is worthy of note that one of the samples of water from the boring contained a small amount of barium in the presence of a large amount of sodium carbonate; in this case the barium must therefore itself have been present as bicarbonate.

Water containing barium chloride to the extent of about 9 grains per 100,000 has recently been found at Llangammarch, in Breconshire.

Since the publication of my original paper on the occurrence of barium sulphate in the Bramcote sandstone, I have continued my examination of samples of sandstone from the basement of the pebble beds of the Bunter, with the object of ascertaining whether the occurrence of barium, either as sulphate or in other forms of combination, was characteristic of the sandstones of that geological period. I have thus far failed to find any similar rock to that at Brancote, and it therefore seems probable that the occurrence of barium sulphate, although it extends over a very extensive area at Bramcote and Stapleford, must be looked upon as being due to purely local causes.

[*February* 22.—Mr. J. Lomas, in a letter dated 20th instant, draws my attention to a paper read by him and Mr. C. C. Moore before the Liverpool Geological Society, on February 8th, 1898, in which the authors draw attention to the occurrence of large proportions of crystallised barium sulphate in triassic sandstones at Prenton and Bidston. Mr. Lomas had previously mentioned the presence of the sulphate in the Bidston sandstone thirteen years ago in a paper to the above Society.

In different specimens of the sandstone the percentage of the sulphate varied from 12·4 to 33·8 per cent. It is colourless and highly crystalline, and is adherent to the sand grains in such a way as to show that it has been deposited *in situ* subsequently to the sand grains. Mr. Lomas states that the occurrence of barytes in the trias is fairly common, and mentions the following localities in which its presence is well known:—Beeston, Alderley Edge, Oxton, Storeton, and Peakstones Rock, Alton. The sulphate is also stated to occur at West Kirby, in Cheshire, and elsewhere as a joint filling, the joints often standing out from the surface of the rock, owing to the resistance of the sulphate to weathering].—F. C.

* A Paper read before the Royal Society, February 23, 1899.

MICROSCOPIC DETECTION OF THE PERCHLORATE IN CHILI SALTPETRE.

By M. VAN BREUKELEVEEN.

According to Behrens when we treat the solution of a perchlorate with chloride of rubidium, a precipitate of perchlorate of rubidium is formed in the form of rhombohedric crystals; it is only slightly soluble. It is on this reaction that the author bases a method enabling him to detect 0·6 per cent of perchlorate of potash in the saltpetre.

Ten grms. of saltpetre are dissolved in 10 c.c. of boiling water, add 50 c.c. of 95 per cent alcohol and boil, allow to cool for one or two hours. Decant the clear liquid, evaporate to dryness, and take up the residue with as small as possible a quantity of water. On this solution we try Behrens's reaction. It must be very slightly coloured by means of a drop of permanganate of potash, and one drop of the liquid is placed under the microscope, in order to search for the characteristic crystals of the perchlorate of rubidium.

It is essential that the solution should be hardly coloured rose-colour, or else the crystals of perchlorate of rubidium might be confounded with those of permanganate of rubidium, which are of a deep red colour.—*Chem. Zeit.*, 1898, p. 145.

ON THE REDUCIBILITY OF METALLIC OXIDES.

By HENRI HELIER.

At one of the recent meetings of the Société Chimique MM. Wyrouboff and Verneuil showed that the oxides of the rare earths polymerise with great facility, and called attention to the fact that many oxides of the ordinary metals behave in the same manner, giving polymers of the general formula $(R_nO_p)_q$, which, far from having q times the basicity of the oxide R_nO_p, are often neutral or even acid. I share their views entirely on this subject. It is for this reason that the oxide of iron, Fe_2O_3, which has not been heated above 450° C. is basic, since it gives ferric sulphate on dissolving in sulphuric acid, while after being heated to above a dull red heat it becomes neutral and is polymerised. It then no longer dissolves in sulphuric acid. Its formula should now be written $(Fe_2O_3)_n$.

It often happens that reactions, impossible with the polymerised molecule, are possible under the same conditions with the simple molecule.

For example, let us heat litharge to the temperature of 350° in a current of hydrogen. The solid body becomes brown and loses oxygen, but the reduction is never complete. As we increase the temperature the loss of oxygen becomes greater and greater, and that in a continuous manner; this, by the way, makes it apparent to me that the existence of a suboxide is hardly possible.

If instead of the oxide we have to do with a neutral compound such as the carbonate, the reduction by means of hydrogen is then perfectly easy; at a temperature of 325° and upwards it is complete.

From this I think we may draw the following conclusions:—

1. That litharge is a polymer with the formula $(PbO)_n$, which, when reduced by hydrogen, decomposes successively into $Pb_1(PbO)_{n-1}$, then to $2Pb_1(PbO)_{n-2}$, &c.

2. That the simple type PbO should be sought for in the only neutral salts, such as the carbonate.

3. That the reduction of the simple oxide PbO is infinitely more easy to effect than the reduction of the polymerised molecule.

If, however, from these few experiments with oxide of lead, we could rise to more general considerations, we should say that the reduction of metallic oxides should always be considered to be more easy when starting with neutral salts. This view is corroborated by the results of experiments; we know, in fact, that in metallurgy we always make carbon react on the neutral mixtures obtained by adding silica to the basic mineral, or carbonate of lime to the acid mineral; these are neutral mixtures which, under the influence of temperature, give birth to neutral compounds.—*Bull. Soc. Chim.*, Series 3, vol. xxi.-xxii., No. 2.

ESTIMATION OF THE PERCHLORATE IN CHILI SALTPETRE.

By C. AHRENS and P. HETT.

The following method will be found sufficiently rapid and exact for commercial analysis:—

Twenty grms. of the well powdered substance are placed in a platinum crucible and moistened with 2 or 3 c.c. of a cold saturated solution of carbonate of soda, add 1 grm. of binoxide of manganese free from chlorine and evaporate to dryness. The mass is brought to fusing point, and the crucible, which must be well covered, is kept at a red heat for fifteen minutes. The product of this fusion is, after cooling, dissolved in 100 c.c. of boiling water, the solution is cooled and made up to 250 c.c.; of this when filtered 50 c.c. are taken (equal to 4 grms. of the sample), acidulate with 10 or 15 c.c. of nitric acid of 1·2 density, then add a 1 per cent solution of permanganate of potash until the red colour lasts for at least a minute. We then add ferrous sulphate and titrate the solution by Volhard's method.

The chlorine is also determined in 4 grms. of the sample by Volhard's method. From the difference between the number of c.c. of decinormal argentic solution employed after fusion, and the number obtained before fusion we calculate the chlorine which exists in the saltpetre in the state of perchlorate.

The addition of carbonate of soda before fusion is simply to prevent the partial volatilisation of the hydrochloric acid. The addition of the binoxide of manganese facilitates the decomposition of the perchlorate; and finally the treatment with permanganate has for its object the elimination of the nitrous acid, and the transformation into iodate, of the small quantity of iodine which is present in the sample in the state of iodide.—*Zeits. für. Offentl. Chem.*, iv., p. 445.

ON A NEW METHOD FOR THE ELECTROLYTIC PRODUCTION OF CHLORATES, BROMATES, IODATES, AND HYPOCHLORITES.

By WILHELM VAUBEL.

According to the process patented by Schuckert and Co. (German patent, No. 13,536), relating to the electrolysis of the alkaline chlorides, the return, in chlorate, is augmented when the liquid in the anodic compartment is kept alkaline by the addition of 1 to 5 per cent of carbonate of potash or soda. Under these conditions we not only prevent the formation of a caustic alkali at the point of contact of the easily attacked carbon anodes, but we also obtain a greater return of chlorine, since the electric conductivity of the caustic alkalis is decidedly higher than that of the corresponding chlorates and carbonates.

In making further researches I found that, on the one hand, by making use of a diaphragm, and on the other hand using bicarbonate of soda as the anodic solution, and the alkaline chloride as the cathodic solution, all the

chlorine which is carried to the anode is transformed into chlorate, and not a trace of chloride is formed. The reaction may be expressed by the following equation:—

$$\overset{-}{Cl}\overset{+}{Na}+\overset{-}{H}\overset{+}{C}O_3=6NaClO_3+6\overset{+}{C}O_2+6\overset{-}{Na}+3H_2O.$$

In this equation, the bodies disengaged at the anode are marked +, and those carried to the cathode −.

It remains to determine in what manner the percarbonic acid formed participates in this reaction through the intermediate compounds.

In this equation, the same as in all other methods for the electrolytic production of chlorates, six atoms of sodium are disengaged, for one molecule of chlorate formed:—$Cl_6+6NaOH=5NaCl+NaClO_3+H_2O$. But in my process this sodium can be recovered in the state of caustic soda. Further, at the anode we obtain a chlorate which is almost entirely free from chloride. As for the carbonic acid which is given off, it can be collected in a solution of carbonate of soda forming bicarbonate.

The working conditions remain the same as in the ordinary methods. The electrolysis is carried on at from 60° to 70° C., that is to say at a temperature which is not high enough to decompose the bicarbonate to any appreciable extent. The density of the current may vary from 5 to 10 ampères per square decimetre. It may be mentioned that the greater the current the higher the return. In the greater number of my experiments the electromotive force was kept between 4 and 5 volts; in some it was a little higher on account of the greater resistance of the diaphragm.

The anodic solution consisted of a saturated solution of bicarbonate of soda or potash. When the action of the current represented 4 ampère-hours, 5 grms. of bicarbonate of soda were added per 100 c.c. of solution; this addition was decreased a little towards the end of the operation. The electrolysis gave a solution of 6·5 grms. of chlorate of soda for every 7·5 grms. of bicarbonate of soda. We found that it was useless to try to increase this return by prolonging the action of the current, for then the useful effect of the current diminishes with great rapidity. At the commencement of the electrolysis the cathode compartment contained a saturated solution of sea salt. At the end of the electrolysis it contained a 10 per cent solution of caustic soda with a very small quantity of sea salt.

The quantities of chlorate of soda obtained are the following:—

For	2	ampère-hours	.. ..	0·36 grm.	$NaClO_3$.
,,	6	,,	.. ..	1·03	,,
,,	10	,,	.. ..	2·62	,,
,,	14	,,	.. ..	4·23	,,
,,	18	,,	.. ..	5·84	,,
,,	26	,,	.. ..	7·92	,,
,,	34	,,	.. ..	11·22	,,
,,	38	,,	.. ..	12·90	,,

According to Oettel's researches (*Zeits. Elect*, 1895, p. 354), by using an electromotive force of 3·3 volts and admitting a useful current effect of 52 per cent, we should obtain a return of 88·14 grms. of chlorate of potash per effective horse-power-hour of 746 watts. The production of 1 kilogrm. of chlorate of potash would therefore require, under the same working conditions, an electromotive force of 11·5 volts. But it must be remembered that Oettel operated on a slightly alkaline solution of the chloride, and without a diaphragm.

In Gall and Montlaur's process, which is now being carried on commercially, a diaphragm is used and the alkaline solution is added at regular intervals to the anodic compartment. The electromotive force being the same as in my process, we will here admit that the production of 88·14 grms. of chlorate of potash corresponds to an expenditure of 1003·5 watts, supposing the density of the current is the same as that recommended by Oettel. Now by my process the production of 88·14 grms. of chlorate of potash only requires the expenditure of 951·91 watts. And further I must repeat that I obtain a solution of caustic alkali at the cathode. If we use carbonate of soda or carbonate of potash, which are always easily transformed into bicarbonate by the carbonic acid given off during the electrolysis, it can be easily seen that my process compares very favourably with those actually in use.

The working conditions are the same for chlorate of soda and for chlorate of potash. By means of this process we can equally well prepare the alkaline bromates and iodates in a very satisfactory state of purity. I must remark that I have not tried any experiments to determine whether this method gives rise to the formation of more or less large quantities of perchlorates, perbromates, &c. By working at a low temperature we obtain hypochlorites instead of chlorates. But here again the product obtained is almost entirely free from chloride. The hypochlorite solutions thus obtained are less stable on heating; it would therefore seem that this stability depends on the presence of the chloride.

The bicarbonates of soda and potash cannot be replaced by the corresponding carbonates, or chlorides will be formed at the same time as the chlorates. Nor can the bicarbonates of soda and potash be replaced by that of ammonia, as it is decomposed by heat; further electrolysis in the cold under these conditions gives chloride of nitrogen.

Before closing I will mention a few experiments I made in which I endeavoured to utilise the oxidising properties of the bicarbonate when submitted to electrolysis.

1. Ferrocyanide of potassium is easily transformed into ferricyanide with the formation of Prussian blue at the anode.

2. Hydrate of baryta is not oxidised; but, on the contrary, hydrate of chromium is easily; anyhow in this case the useful effect of the current is only 3 per cent, while Hœussermann obtained a useful effect of 47 per cent by electrolysing hydrate of chromium in suspension in an excess of caustic soda.

3. Experiments made with a view to the electrolytic preparation of fluorates by the same method gave no results.—*Chemiker Zeitung*, 1898, No. 34, p. 331.

THE ESTIMATION OF BORIC ACID.*

By F. A. GOOCH AND LOUIS CLEVELAND JONES.

(Concluded from p. 100).

The Use of Calcium Oxide as a Retainer (continued).

If we take into consideration, therefore, the inevitable inaccuracy and inconvenience of Thaddeeff's proposal, it cannot be regarded as a desirable substitute for the process according to which boric acid is absorbed and retained for weighing with calcium oxide, especially since the difficulties in the way of getting constant weights of that substance are by no means insuperable.

Thus the following table shows the series of weights taken in several experiments in bringing calcium oxide to a constant weight in a 50 c.m.³ platinum crucible ignited over a blast lamp, as well as the weight taken after adding a known amount of standard boric acid solution to the slaked oxide, evaporating, and igniting. The results recorded are those of experiments made on days not moist beyond the average, and with the greatest care to approach the limit of accuracy with which calcium oxide and the boric acid held thereby can be weighed under ordinarily favourable conditions. The first weight of calcium oxide recorded under each experiment was taken after a strong ignition over the blast lamp for about one-half hour. The succeeding weights were taken after similar ignition

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vii, 1899,

of five minutes. In all cases the crucible was left to stand a definite period in a sulphuric acid desiccator, and, after the approximate value had once been obtained, the weights of the preceding weighing were replaced on the balance before the crucible was taken from the desiccator. The average of the weights bracketed is the weight taken as constant for the calculations.

	CaO taken.	B_2O_3 taken.	$CaO+B_2O_3$ taken.	$CaO+B_2O_3$ found.		Error.
	Grm.	Grm.	Grm.	Grm.		Grm.
1.	0·9505 0·9493 0·9493	0·9493	0·2095	1·1590 1·1591	1·1591	+0·0003
2.	1·1319 1·1317 1·1313 1·1315	1·1315	0·2150	1·3499 1·3474 1·3475 1·3276	1·3475	+0·0010
3.	0·8028 0·8025 0·8024	0·8024	0·1184	0·9205 0·9206 0·9206	0·9206	+0·0002
4.	2·6980 2·6975 2·6973 2·6973	2·6973	0·2073	2·9043 2·9049 2·9044	2·9048	+0·0002

Obviously calcium oxide may be weighed with accuracy, with or without boric acid; but the fact remains that a less hygroscopic absorbent—one requiring less care in the handling—is to be desired.

The Use of Sodium Tungstate as a Retainer.

In searching for a suitable material of less hygroscopicity to replace calcium oxide as a retainer for boric acid, we have found that sodium tungstate, fused with a slight excess of tungstic acid over that contained in the normal tungstate to insure its freedom from carbonate), answers this purpose excellently. This substance is definite in weight, not hygroscopic, soluble in water, and recoverable in its original weight after evaporation and ignition. To test its value as a retainer for boric acid, portions of it—4 to 7 grms.—were fused and weighed in a 50 c.m.³ crucible, the tungstate was dissolved in water, and to it was added a known amount of a standard solution of boric acid. After diluting, mixing, evaporating, and fusing the residue, the increase in weight should represent the boric anhydride held by the tungstate. The results of the accompanying table show how accurately the boric acid is retained under these conditions. In Experiments 3 to 7 the tungstate, after its first weighing, was dissolved, transferred to a larger platinum dish, and mixed therein with the boric acid. After evaporation to a suitable volume this solution of tungstate and boric acid was transferred to the original crucible for final evaporation and ignition.

$Na_2WO_4+WO_3$ taken.	B_2O_3 taken.	B_2O_3 found.	Error in B_2O_3.
Grm.	Grm.	Grm.	Grm.
6·5416	0·1784	0·1771	−0·0013
7·3134	0·1786	0·1773	−0·0013
5·5003	0·0950	0·0952	+0·0002
4·1394	0·0944	0·0944	0·0000
7·5037	0·2148	0·2149	+0·0001
4·7744	0·2718	0·2702	−0·0016
6·6470	0·2503	0·2487	−0·0016

It is plain that, though the sodium tungstate does not hold the boric acid with absolute accuracy, the errors are not unreasonable, −0·0008 grm. in the mean. Upon substituting the tungstate for calcium oxide as a retainer in the distillation process, the results were likewise highly favourable.

We used by preference the apparatus originally proposed, excepting that the Erlenmeyer flask used as a receiver is fitted tightly to the condenser and trapped with water bulbs. The retort is made very easily from a 150 c.m.³ pipette, and has the special advantage that particles of the residue spattering during distillation are easily washed from the walls of the vessel by a slight rotary motion of the retort. It was found that special care should be taken to give the tungstate ample time for contact with the distillate before exposing the latter to atmospheric evaporation. The distillate was received, therefore, in a dilute solution of sodium tungstate placed in the receiver, cooled by ice and trapped with water, and the mixture was well stirred, allowed to stand one-half hour, evaporated to small volume in a large dish, and transferred to the crucible in which the tungstate had been originally weighed. After thorough drying, the residue was ignited to fusion and weighed. When acetic acid was employed in the retort, care was taken in the ignition to expose the fused mass freely to the air (by causing it to flow upon the sides of the crucible) until the colour of the cooled tungstate was white, in order that the reducing effect of the acetate might be eliminated. In the experiments recorded in the following table the tungstate was used in the receiver to retain the boric acid distilled as usual with methyl alcohol, from the borates treated with acetic acid, nitric acid, or sulphuric acid, in amounts regulated by the use of phenolphthalein as an indicator.

$Na_2WO_4+WO_3$ taken.	B_2O_3 taken.	B_2O_3 found.	Error.
Grm.	Grm.	Grm.	Grm.
	With Nitric Acid.		
8·5516	0·1582	0·1572	−0·0010
4·9639	0·1329	0·1323	−0·0006
8·0033	0·1267	0·1256	−0·0011
	With Acetic Acid.		
4·9658	0·1434	0·1418	−0·0016
6·0289	0·1431	0·1433	+0·0002
4·6797	0·1589	0·1587	−0·0002
4·0013	0·1433	0·1422	−0·0011
	With Sulphuric Acid.		
6·3439	0·1582	0·1579	−0·0003
8·8227	0·1582	0·1577	−0·0005
10·1516	0·1265	0·1264	−0·0001
6·5738	0·1392	0·1390	−0·0002

Excessive use of acid is disadvantageous, and this is especially true in the case of sulphuric acid; for if this acid is carried over with the methyl alcohol, as it is at 100° if present in appreciable excess, a part of it, at least, is held permanently by the tungstate to increase the apparent weight of the boric acid to be estimated.

The manipulation of the tungstate presents no difficulties, and the results obtained by its use are reasonably accurate.

ON THE

SEPARATION OF IRON FROM ZIRCONIUM AND CERTAIN OTHER ALLIED METALS.*

By J. MERRITT MATTHEWS.

(Concluded from p. 99).

As thorium, cerium, and titanium belong to the same group as zirconium, and form corresponding hydrated oxychlorides insoluble in ether, the same method was applied in the separation of iron from these metals as with zirconium, and very good results were obtained. The method was carried out in every particular as already described, and was also extended to include lanthanum, neodymium, and praseodymium, as their hydrated chlorides were found to be insoluble in ether.

* *Journal of the American Chemical Society*, xx., No. 11, Nov., 1898.

Thorium from Iron.

The thorium salt used was the chloride, and its analysis gave 60·79 per cent thorium dioxide, and was not appreciably contaminated with iron, so no correction was necessary in the percentages found.

I. 0·5608 grm. thorium tetrachloride with 0·2246 grm. ferric chloride gave :—
0·3418 grm. thorium dioxide = 60·95 per cent thorium dioxide.
0·0657 grm. ferric oxide = 29·25 per cent ferric oxide.

II. 0·2681 grm. thorium tetrachloride with 0·4625 grm. ferric chloride gave :—
0·1628 grm. thorium dioxide = 60·72 per cent thorium dioxide.
0·1364 grm. ferric oxide = 29·53 per cent ferric oxide.

III. 0·5072 grm. thorium tetrachloride with 0·3217 grm. ferric chloride gave :—
0·3075 grm. thorium dioxide = 60·63 per cent thorium dioxide.
0·0952 grm. ferric oxide = 29·59 per cent ferric oxide.

IV. 1·0368 grm. thorium tetrachloride with 0·7241 grm. ferric chloride gave :—
0·6318 grm. thorium dioxide = 60·94 per cent thorium dioxide.
0·2137 grm. ferric oxide = 29·51 per cent ferric oxide.

V. 0·1193 grm. thorium tetrachloride with 0·6976 grm. ferric chloride gave :—
0·0720 grm. thorium dioxide = 60·35 per cent thorium dioxide.
0·2062 grm. ferric oxide = 29·58 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·25	29·53	29·59	29·51	29·58
Thorium dioxide ..	60·79	60·95	60·72	60·63	60·94	60·35

Cerium from Iron.

Cerium chloride was used, and its analysis gave 61·11 per cent cerium dioxide.

I. 0·1098 grm. cerium chloride with 0·3510 grm. ferric chloride gave :—
0·0669 grm. cerium dioxide = 60·93 per cent cerium dioxide.
0·1044 grm. ferric oxide = 29·74 per cent ferric oxide.

II. 0·1930 grm. cerium chloride with 0·2574 grm. ferric chloride gave :—
0·1178 grm. cerium dioxide = 61·04 per cent cerium dioxide.
0·0758 grm. ferric oxide = 29·45 per cent ferric oxide.

III. 0·2240 grm. cerium chloride with 0·2642 grm. ferric chloride gave :—
0·1367 grm. cerium dioxide = 61·03 per cent cerium dioxide.
0·0784 grm. ferric oxide = 29·67 per cent ferric oxide.

IV. 0·7532 grm. cerium chloride with 0·1024 grm. ferric chloride gave :—
0·4598 grm. cerium dioxide = 61·05 per cent cerium dioxide.
0·0301 grm. ferric oxide = 29·39 per cent ferric oxide.

V. 0·1262 grm. cerium chloride with 0·8436 grm. ferric chloride gave :—
0·0774 grm. cerium dioxide = 61·33 per cent cerium dioxide.
0·2489 grm. ferric oxide = 29·52 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29 74	29·45	29·67	29·39	29·52
Cerium dioxide ..	61·11	60·93	61·04	61·03	61·05	61·33

Titanium from Iron.

Titanium chloride was the salt used, and on analysis this gave 57·17 per cent titanium dioxide.

I. 0·1060 grm. titanium chloride with 0 2224 grm. ferric chloride gave :—
0·0604 grm. titanium dioxide = 56·98 per cent titanium dioxide.
0·0660 grm. ferric oxide = 29·68 per cent ferric oxide.

II. 0·2588 grm. titanium chloride with 0 2508 grm. ferric chloride gave :—
0·1474 grm. titanium dioxide = 56·95 per cent titanium dioxide.
0·0736 grm. ferric oxide = 29·35 per cent ferric oxide.

III. 0·6532 grm. titanium chloride with 0·1086 grm. ferric chloride gave :—
0·3728 grm. titanium dioxide = 57·08 per cent titanium dioxide.
0·0318 grm. ferric oxide = 29·28 per cent ferric oxide.

IV. 0·3549 grm. titanium chloride with 0·7643 grm. ferric chloride gave :—
0·2033 grm. titanium dioxide = 57·28 per cent titanium dioxide.
0·2253 grm. ferric oxide = 29·48 per cent ferric oxide.

V. 0·1083 grm. titanium chloride with 0·9212 grm. ferric chloride gave :—
0·0617 grm. titanium dioxide = 56·97 per cent titanium dioxide.
0·2720 grm. ferric oxide = 29·53 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·68	29·35	29·28	29·48	29·53
Titanium dioxide .	57·17	56·98	56·95	57·08	57·28	56 97

Lanthanum from Iron.

The lanthanum chloride used in the analyses gave 50·20 per cent lanthanum oxide, La_2O_3.

I. 0·2968 grm. lanthanum chloride with 0·1465 grm. ferric chloride gave :—
0·1485 grm. lanthanum oxide, La_2O_3, = 50·03 per cent lanthanum oxide.
0·0435 grm. ferric oxide = 29·69 per cent ferric oxide.

II. 0·4541 grm. lanthanum chloride with 0·7105 grm. ferric chloride gave :—
0·2274 grm. lanthanum oxide, La_2O_3, = 50·08 per cent lanthanum oxide.
0·2098 grm. ferric oxide = 29·53 per cent ferric oxide.

III. 0·1079 grm. lanthanum chloride with 0·6514 grm. ferric chloride gave :—
0·0539 grm. lanthanum oxide, La_2O_3, = 49·95 per cent lanthanum oxide.
0·1926 grm. ferric oxide = 29·57 per cent ferric oxide.

IV. 0·7525 grm. lanthanum chloride with 0·1024 grm. ferric chloride gave :—
0·3769 grm. lanthanum oxide, La_2O_3, = 50·09 per cent lanthanum oxide.
0·0304 grm. ferric oxide = 29·68 per cent ferric oxide.

V. 0·5048 grm. lanthanum chloride with 0·5025 grm. ferric chloride gave :—
0·2539 grm. lanthanum oxide, La_2O_3, = 50·30 per cent lanthanum oxide.
0·1485 grm. ferric oxide = 29·55 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide	29·44	29·69	29·54	29 57	29·68	29·55
Lanthanum oxide, La_2O_3	50·20	50·03	50·08	49·95	50·09	50·30

Praseodymium from Iron.

The salt used was praseodymium nitrate, and its analysis gave 43·33 per cent praseodymium oxide, Pr_2O_3.

I. 0·5308 grm. praseodymium nitrate with 0·4245 grm. ferric chloride gave :—
0·2293 grm. praseodymium oxide, Pr_2O_3, = 43·20 per cent praseodymium oxide.

0·1261 grm. ferric oxide = 29·70 per cent ferric oxide.

II. 0·5090 grm. praseodymium nitrate with 0·3596 grm. ferric chloride gave :—

0·2198 grm. praseodymium oxide, Pr_2O_3, = 43·18 per cent praseodymium oxide.

0·1064 grm. ferric oxide = 29·59 per cent ferric oxide.

III. 0·1085 grm. praseodymium nitrate with 0·7240 grm. ferric chloride gave.—

0·0465 grm. praseodymium oxide, Pr_2O_3, = 42·86 per cent praseodymium oxide.

0·2139 grm. ferric oxide = 29·54 per cent ferric oxide.

IV. 0·6849 grm. praseodymium nitrate with 0·1096 grm. ferric chloride gave :—

0·2960 grm. praseodymium oxide, Pr_2O_3, = 43·33 per cent praseodymium oxide.

0·0323 grm. ferric oxide = 29·43 per cent ferric oxide.

V. 0·2532 grm. praseodymium nitrate with 0·2485 grm. ferric chloride gave :—

0·1092 grm. praseodymium oxide, Pr_2O_3, = 43·13 per cent praseodymium oxide.

0·0735 grm. ferric oxide = 29·58 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide		29·44	29·70	29·59	29·54	29·43	29·58
Praseodymium oxide, Pr_2O_3		43·33	43·20	43·18	42·86	43·22	43·13

Neodymium from Iron.

Neodymium nitrate was used, and its analysis gave 42·20 per cent neodymium oxide, Ne_2O_3.

I. 0·1763 grm. neodymium nitrate with 0·4286 grm. ferric chloride gave :—

0·0740 grm. neodymium oxide, Ne_2O_3, = 41·97 per cent neodymium oxide.

0·1261 grm. ferric oxide = 29·42 per cent ferric oxide.

II. 0·6389 grm. neodymium nitrate with 0·1842 grm. ferric chloride gave :—

0·2688 grm. neodymium oxide, Ne_2O_3, = 42·07 per cent neodymium oxide.

0·0540 grm. ferric oxide = 29·32 per cent ferric oxide.

III. 0·7246 grm. neodymium nitrate with 0·7562 grm. ferric chloride gave :—

0·3051 grm. neodymium oxide, Ne_2O_3 = 42·11 per cent neodymium oxide.

0·2229 grm. ferric oxide = 29·48 per cent ferric oxide.

IV. 0·1545 grm. neodymium nitrate with 0·2046 grm. ferric chloride gave :—

0·0645 grm. neodymium oxide, Ne_2O_3, = 41·75 per cent neodymium oxide.

0·0610 grm. ferric oxide = 29·81 per cent ferric oxide.

V. 0·2081 grm. neodymium nitrate with 0·7680 grm. ferric chloride gave :—

0·0869 grm. neodymium oxide, Ne_2O_3, = 41·76 per cent neodymium oxide.

0·2271 grm. ferric oxide = 29·57 per cent ferric oxide.

	Used.	Found. I.	II.	III.	IV.	V.
Ferric oxide		29·44	29·42	29·32	29·48	29·81	29·57
Neodymium oxide, Ne_2O_3		42·20	41·97	42·07	42·11	41·75	41·76

The praseodymium and neodymium salts existing originally as nitrates, were evaporated to dryness with hydrochloric acid in order to convert them into the chloride form.

General Remarks.

Gooch and Havens, in the *American Journal of Science* for December, 1896 (see also Chemical News, vol. lxxiv., p. 296), describe a method for the separation of aluminum from iron by treatment with anhydrous ether saturated with hydrochloric acid gas. The hydrated chloride of aluminum remains insoluble, whereas the ferric salt is completely dissolved. This method is practically the same as the one herein described for the separation of iron from zirconium and the other rare earths; but the results of this present research were mostly obtained in October and November, 1896, before the writer was aware of the contemporaneous work of Gooch and Havens. These latter writers also describe a separation of aluminum from glucinum by the same method (*Am. Journ. Sci.*, August, 1897).

The use of absolute ether may militate somewhat against the practical application of this method to general analytical purposes; since in the case of most of the metals experimented upon, very good separations are already known which do not require the use of a reagent both difficult and unpleasant to manipulate. This method, however, is especially recommended for the separation of iron from zirconium, the separations of the other metals being only tried as a matter of interest through the analogy existing between those metals and zirconium. A point, however, which may prove of practical importance, and which it is most desirable to emphasize here, is that by carefully following out the procedure herein described, zirconium oxychloride and dioxide may be easily and quickly prepared perfectly free from iron. This fact may be of considerable importance and utility in the preparation of zirconium compounds for use in atomic weight determinations, where a high degree of purity is absolutely necessary in order to obtain authentic results.

THE

DETERMINATION OF SULPHUR IN ASPHALT.*

By E. H. HODGSON.

The numerous articles recently published on the analysis and chemistry of asphalts, and the wide range of opinion as to the relative values of the different methods in use for the determination of sulphur, have led me to make a comparison of results on some typical asphalts.

Dr. E. H. Miller, through the kindness of Mr. A. W. Dow, of Washington, was enabled to secure samples, the sources and natures of which were known. The samples were labelled Trinidad Lake, Trinidad Crude, Trinidad Lake Refined, Cuban Crude, Alcatraz Crude, and California Crude, and were described by Mr. Dow as follows :—

Trinidad Lake.—Asphalt from the lake on the island of Trinidad, imported by Barber Asphalt Co. for paving.

Trinidad Crude. — Crude asphalt from Hadley's Diggings, about one mile from Trinidad Lake. It is known as "iron pitch," being the hardest asphalt found in Trinidad.

Trinidad Lake Refined.—This is crude Trinidad Lake asphalt melted up to drive out the water.

Alcatraz Crude.—From Ventura Co., California, used by the Alcatraz Asphalt Co. for paving, after the addition of liquid asphalt.

California Crude.—From Kern Co., California, used by the Standard California Asphalt Co. for paving, after the addition of liquid asphalt.

Sample "Trinidad Lake" was found to lose water very rapidly, so it was heated to about 60° C. (not sufficient to melt it) and then remained constant.

The samples were ground as fine as possible in a mortar, and then placed in glass bottles fitted with tight corks. From these bottles average samples were taken and kept in test-tubes for use.

Heating with Strong Nitric Acid in a Sealed Tube—Carius's Method.

The tubes were made in the usual way from heavy glass

* Contributions from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xx., No. 11.

tubing. Two determinations were made on each sample. One on ½ grm. and one on ¾ grm. A general description of the method is as follows:—One-half grm. of asphalt is introduced into the bottom of the tube, and 15 c.c. of fuming nitric acid (1·60 sp. gr.) is poured upon it. The open end of the tube is then drawn out into a thick-walled fine-calibre tube, but not sealed. The tube is then heated for about six hours in a water-bath kept at 80—90° C. Then 5 c.c. more acid are added, the tube is sealed, and heated in a guarded furnace at a temperature of about 150° C. for from four to five hours. Allow the tube to cool, then open and re-seal, and re-heat for from two to four hours at a temperature of 180—200° C. Cool, open, and remove the liquid and residue into a No. 2 beaker. Dilute with water, filter, and wash. If the residue contains anything but sand it is saved and treated separately. The filtrate is evaporated to dryness on the water-bath, adding a piece of solid sodium hydroxide. The nitric acid is driven out by repeated evaporation of the solution, with the addition of hydrochloric acid, and the silica dehydrated in an air-bath at 110—115° C. Cool the dehydrated mass, add 2 to 3 c.c. of hydrochloric acid and 100 c.c. of water, stir well, filter, and wash well with hot water. Dilute the filtrate to about 200 c.c., heat to boiling, and while boiling add 20 c.c. of barium chloride (20 per cent solution), drop by drop, from a burette, at the rate of about a drop a second. Stir all the time. Boil the solution about ten minutes, and allow it to stand twenty-four hours. Filter, wash with hot water, and ignite. Treat with sulphuric acid, and re-ignite. Then cool and weigh the barium sulphate. A pure white product was obtained, and the precipitate did not run through the filter.

The residue from the sealed tube, if not thoroughly oxidised, is fused with 6 grms. of mixed carbonates and 1 grm. of potassium nitrate. The fusion is dissolved in water and hydrochloric acid. The nitrates are destroyed by evaporating with the addition of hydrochloric acid, and the silica dehydrated as before. Filter off the silica and wash. Then determine the sulphuric acid in the filtrate as before described.

When ¾ grm. of asphalt was used, 25 c.c. of fuming nitric acid were employed instead of 20 c.c.

The following results were obtained:—

Trinidad Lake.

	Weight of barium sulphate. Grm.	Sulphur. Per cent.
One-half grm.	0·1526	4·192
Residue	0·0051	0·140
		4·332
Three-fourths grm.	0·2238	4·10
Residue	0·0068	0·18
		4·28

Trinidad Crude.

One-half grm.	0·1249	3·400
Residue	0·0034	0·086
		3·486
Three-fourths grm.	0·1720	3·148
Residue	0·0106	0·19
		3·338

Trinidad Lake Refined.

One-half grm.	0·1585	4·35
Residue	—	—
		4·35
Three-fourths grm.	0·2160	4·21
Residue	0·0137	0·25
		4·46

	Weight of barium sulphate. Grm.	Sulphur. Per cent.
Cuban Crude.		
One-half grm.	0·1315	3·61
Residue	—	—
		3·61
Three-fourths grm.	No results.	
Alcatraz Crude.		
One-half grm.	0·1839	5·05
Residue	0·0195	0·54
		5·59
Three-fourths grm.	0·2749	5·12
Residue	0·0294	0·46
		5·58
California Crude.		
One-half grm.	0·2589	7·11
Residue	0·0145	0·398
Three-fourths grm.	No results.	

Deflagration Method—S. F. and H. E. Peckham.

A porcelain crucible is heated to a dull red heat, and *small* amounts of a mixture of 1 grm. finely ground asphalt, 8 grms. of potassium nitrate, and 8 grms. of mixed sodium and potassium carbonates added from time to time, just keeping the material in the crucible melted. When all of the mixture has been added, heat to perfect fusion with a blast lamp, and cool. Dissolve the fusion in 20 c.c. hydrochloric acid and 40 c.c. of water, and wash the crucible well with hot water. The solution is evaporated down to dryness, dehydrated at 110—115°, the silica filtered off, and the sulphuric acid determined in the filtrate as before. The results are as follows:—

Trinidad Lake.

No.	Weight of barium sulphate. Grm.	Sulphur. Per cent.
1.	0·2770	3·804
2.	0·2689	3·68
Trinidad Crude.		
1.	0·2443	3·37
2.	0·2359	3·24
Trinidad Lake Refined.		
1.	0·2634	3·62
2.	—	—
Cuban Crude.		
1.	0·2009	2·76
2.	0·2052	2·82
Alcatraz Crude.		
1.	0·3054	4·19
2.	0·2773	3·81
California Crude.		
1.	0·4376	6·50
2.	—	—

Sodium Peroxide Method.

Place 1 grm. of the fine asphalt in the bottom of a large nickel crucible. Cover with a layer of about 4 grms. of mixed carbonates and about 1 grm. of solid sodium hydroxide. Cover the crucible and heat gently until the gases are driven off. Then raise the heat and add small amounts of sodium peroxide from time to time, until no further action is noticed on the addition of fresh Na_2O_2. Then, with the blast-lamp, heat to perfect fusion. This takes but a few minutes. Pour as much of the fusion as possible upon the cover of the crucible and cool slowly.

Place the fusion, crucible, and cover in a casserole containing 50 c.c. hot water, and after thorough digestion on the water-bath, filter off the residue and wash well with hot water. The filtrate is made acid with hydrochloric acid, and evaporated down to dryness, dehydrated at 110—115° C., the silica filtered off, and the sulphuric acid determined in the filtrate as already described. Results by this method :—

Trinidad Lake.

No.	Weight of barium sulphate. Grm.	Sulphur. Per cent.
1.	0·2687	3·69
2.	0·2744	3·77

Trinidad Crude.

1.	0·2426	3·33
2.	0·2360	3·25

Trinidad Lake Refined.

1.	0·2962	4·07
2.	0·2929	4·02

Cuban Crude.

1.	0·2256	3·10
2.	0·2230	3·06

Alcatraz Crude.

1.	0·2887	3·97
2.	0·2880	3·96

California Crude.

1.	0·4557	6·26
2.	0·4481	6·15

Ignition with Calcined Magnesia—Eschka's Method.

One grm. of finely ground asphalt is intimately mixed with 1 grm. of calcined magnesia and about ½ grm. of dry mixed carbonates is added. Mix well and place in a platinum or porcelain crucible. With the crucible in an inclined position, heat at a dull red heat, stirring every few minutes, until the ash is a dull yellow. Cool, and add about 1 grm. of finely-ground ammonium nitrate, and mix thoroughly. Heat slowly to a dull red, and continue the heating until the ammonium nitrate is entirely decomposed. Cool, extract the mass thoroughly with water (hot water preferred), filter, and wash well. Acidulate the filtrate with hydrochloric acid, and precipitate the sulphuric acid as before described. The results are as follows :—

Trinidad Lake.

No.	Weight of barium sulphate. Grm.	Sulphur. Per cent.
1.	0·2660	3·65
2.	0·2791	3·83

Trinidad Crude.

1.	0·2608	3·58
2.	0·2567	3·53

Trinidad Lake Refined.

1.	0·2744	3·77
2.	0·2650	3·64

Cuban Crude.

1.	0·2020	2·77
2.	0·1941	2·66

Alcatraz Crude.

1.	0·3054	4·19
2.	0·3021	4·16

California Crude.

1.	0·5011	6 88
2.	0·5109	7·01

The relative accuracy of the different methods is best shown by tabulating the results, as follows :—

	Trinidad Lake.	Trinidad Crude.	Trinidad Lake Refined	Cuban Crude.	Alcatraz Crude.	California Crude.
Sealed tube..	4·33	3·49	4·35	3·61	5·59	7·51
	4·28	3 34	4·46	—	5·57	—
Deflagration.	3·80	3·37	3·62	2 82	4·19	6 50
	3·68	3·24	—	2·76	3·81	—
Peroxide ..	3·69	3·33	4·07	3·10	3·97	6·26
	3·77	3·25	4·02	3·06	3·96	6·15
Eschka's ..	3·65	3·58	3·77	2·77	4·19	6·88
	3·83	3·53	3·64	2·66	4·16	7·01

It would appear, therefore, that the "sealed tube" gives the most accurate results, but on account of the explosion of the tubes and the time required for a determination, it would probably be barred out.

The deflagration method apparently gives low results. It is much shorter than the sealed tube, but longer than either the peroxide or Eschka's method.

Of the latter two, the Eschka's method is perhaps the better, as it requires less time and attention to carry out, and gives about as good results.

The peroxide method is shorter than the deflagration method and about as accurate.

The reagents employed were first tested for sulphur.

	Sulphur. Per cent.
The sodium and potassium carbonate contained	0·005
The sodium peroxide contained	0·003

The rest of the reagents were sulphur-free or contained but the merest trace.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 24th, 1899.

Prof. PERRY, F.R.S., Vice-President, in the Chair.

A PAPER by Mr. E. F. J. LOVE, on "*The Joule-Thomson Effect and its Connection with the Characteristic Equation, and some of its Thermo-dynamical Consequences*," was read by Mr. WATSON.

The author points out that the results of the original Joule-Thomson investigation of the thermal effects of fluids in motion have been utilised hitherto almost exclusively for the one purpose of determining the relation between various gas-thermometer scales and the absolute scale of temperature. He proceeds to deduce further consequences from those results, indicating the relation between the formula assigned to the Joule-Thomson effect, regarded as a function of temperature, and the particular form adopted for the characteristic equation of a gas. He further attempts to supply a theoretical basis to the various formulæ of van der Waals, Rose-Innes, and others, at the same insisting upon a very high degree of accuracy for the original experimental work of Joule and Thomson. Then follows a discussion of the relation between the intrinsic energy of a gas and its volume, and a method is given for calculating the ratio of the principal two specific heats of a gas. Lastly, the author considers some points in the thermo-dynamics of substances at their temperature of maximum density. It is shown that (1) the Joule-Thomson effect for every substance at maximum density is zero; just as it is, though for a different reason, in the case of an ideal perfect gas. And (2) that the infinite number of specific heats possessed by every substance are, at the temperature corresponding to maximum density, reduced to one specific heat.

Mr. ROSE-INNES congratulated the author on having written an interesting paper on a difficult subject. At the same time he felt bound to acknowledge that he was out of sympathy with the general idea contained in the paper

The experimental difficulties that occurred in carrying out the Joule-Thomson investigation were so enormous that it was better to rely on them as little as possible, notwithstanding the great skill of the experimenters. The Joule-Thomson results could not be disregarded altogether, since they were necessary for the establishment of the thermo-dynamic scale; but once that scale had been set up, it was better to have recourse as much as possible to such experiments as those of M. Amagat on the compressibility of gases. He also pointed out that one of the deductions given in the paper from van der Waals's formula had already been given by van der Waals himself.

Mr. WATSON replied, and the VICE-PRESIDENT proposed a vote of thanks to the author for his valuable paper. The meeting then adjourned until March 10th.

NOTICES OF BOOKS.

Practical Organic Chemistry for the Elementary and Advanced Examinations of the Science and Art Department. By GEORGE GEORGE, F.C.S. London: W. B. Clive, Correspondence College Press. Pp. 96.

As its name indicates, this book is intended for the use of Students preparing for the examination in Practical Organic Chemistry (Subject XI.) at the Science and Art Department. The author suggests that the student should first perform all the tests given for each substance, and then make up mixtures for himself and endeavour to detect the various ingredients: this would, of course, give him a certain amount of practice, but testing mixtures made by some one else will do far more real good; there is always a tendency to strain a point when you *know* what is present, and unfortunately the average student does not always sufficiently realise that his objective is to learn, and to acquire skill, not to merely solve puzzles and pass examinations.

The book is divided into eight chapters, in which the ordinary organic compounds—such as oxalic, tartaric, benzoic, acetic, carbolic, &c., acids; methyl and ethyl alcohols. sugars, glycerin, urea, &c.—are dealt with, and tests for recognising each given. In the last chapter the preparation of some of the reagents used in organic analysis is given.

The book is handy in size and clearly written, and should be found useful by those for whom it is intended.

A Text-book of Botany. By J. M. LOWSON, M.A., B.Sc., F.L.S. London: W. B. Clive, University Correspondence College Press. Pp. 394.

THE intention of the author in preparing this book was to provide a work that will be an efficient introduction to the subject, and include as well all the types set for the London University Intermediate Science and Preliminary Scientific Examinations.

The first part of the work is devoted to the general facts of structure and physiology; Part II. deals with the angiosperm, its seed, stem, root, leaf, nutrition, fruit, &c.; Part III. is on vascular cryptogams and flowering plants; and Part IV. on the lower cryptogams, such as liverworts and mosses, algæ, and fungi. There is a set of questions at the end of each part.

Royal Institution.—The Friday Evening Discourse on March 17th is on "The Electric Fish of the Nile," by Professor Francis Gotch; and that on March 24th on "Transparency and Opacity," by Lord Rayleigh.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 5, January 30, 1899.

Explosibility of Acetylene at Low Temperatures.—Georges Claude.—The author shows that the solubility of acetylene in acetone increases with great rapidity as the temperature diminishes. At −80°, the temperature at which acetylene freezes, and under atmospheric pressure, acetone dissolves more than two thousand times its volume of gas. A platinum wire heated to redness by an electric current can be kept indefinitely in this solution without explosive decomposition occurring.

Alloys of Iron and Nickel.—F. Osmond.—The transformation points of alloys of iron and nickel have been determined for alloys containing less than 50 per cent of nickel. The author finds the same for alloys containing 50 to 100 per cent of nickel. It is not always easy to find the quantity of heat absorbed during the rise of temperature or given out during cooling. As this is so very small in many cases, the plan has been devised of determining the temperature at which magnetisation of the iron begins during the cooling and disappears during the heating process. The same method has been employed also to determine the transformation points of alloys containing under 50 per cent of nickel; the results being identical with those found by other methods. The author's results are given in a table and plotted on a curve.

Decomposition of Carbonic Oxide in presence of Metallic Oxides.—O. Boudouard.—The author extends his examination of decomposition of carbonic oxide by oxide of iron to oxides of nickel and cobalt. At a temperature of 455°, the same as that used in the former experiments, he finds that the carbonic oxide is totally decomposed by the oxides if the high temperature is maintained for a sufficient time. In the case of oxides of cobalt and nickel, the time necessary to arrive at the same results is shorter than in the case of iron.

A New Method of Estimating Carbonic Oxide.—MM. Schlagdenhauffen and Paget.—Oxides of silver and copper when heated in a current of carbonic oxide are completely reduced—the former at 60°, the latter at 300°—and can consequently be used to absorb the gas quantitatively. As the carbonic acid formed theoretically corresponds to the oxygen lost, it follows that the reaction may be used for the estimation of carbonic oxide.

Certain Iodine Compounds of the Aromatic Ketones.—A. Collet.—Only a small number of the iodine derivatives of the aromatic ketones is known—in particular, methyl-*p*-iodo-phenylketone. The author has obtained an iodo-methyl-phenyl ketone substituted in the methyl-group. The substance is prepared by treating chlorinated or brominated methyl-phenyl ketone in alcoholic solution with finely-powdered potassium iodide at the ordinary temperature. Chloride or bromide of potassium is formed, and the liquid, poured into excess of cold water, yields a crystalline mass, which possesses the composition $C_6H_5COCH_2I$. This body crystallises in colourless needles, which melt at 29°. Analogous substances were prepared in a similar manner, viz., iodo-methyl-*p*-tolyl ketone and iodo-ethyl-*p*-tolyl ketone. The vapours of these ketones exert an irritating effect upon the eyes. They are decomposable by light; their solutions in benzene or carbon bisulphine exposed to direct sunlight, turn rapidly violet, owing to liberation of a small quantity of iodine.

Preparation of Oxyethylamines.—F. Chancel.—Wurtz obtained oxyethylamines by the action of ammonia

on ethylene oxide, and also by reacting with ammonia on glycol chlorhydrin. M. Chancel was able by this method to prepare the hydrochloride of trioxyethylamine not obtained by Wurtz; also the chloro-aurate of this base, the chloroplatinates of mono- and di-oxyethylamine, and the neutral oxylate of mono-oxyethylamine.

Extraction and Synthesis of the Perfume Principle of the Flower of Jasmine.—Albert Verley.—For several years attempts have been made to extract the essential oil of the jasmine flower. This cannot be distilled with steam, since it only exists in the plant in small quantity, and is completely destroyed by prolonged boiling with slightly acidulated water. The author has succeeded in obtaining the perfume in the following manner:—The fresh jasmine flowers, picked in the morning dew, were enclosed in glass cases greased on the interior. The grease absorbed the perfume exhaled by the flowers, the faded ones being replaced by fresh each morning. After some days, the grease was washed with oil of vaseline, which removed the essence. The oil of vaseline was then extracted with acetone, and the latter evaporated *in vacuo*. The residue consisted of an oil, of a clear red colour, which possessed the characteristic odour of jasmine in a greatly intensified degree. This was fractionated under a pressure of 12 m.m. Analysis ascribed the formula $C_9H_{10}O_2$. The body possessed the properties of neither an aldehyde nor a ketone. Oxidation proved the presence of a benzene nucleus in its molecule, and it was finally classed as an acetal. Synthesis of the perfume was effected from phenylglycol and formaldehyde in presence of water and sulphuric acid.

Action of Di-diazochlorides of Benzidine, Orthotoluidine, and Orthodianisidine on Acetylacetone.—G. Favrel.—Not suitable for abstraction.

No. 6, February 6, 1899.

Oxidation of certain Ureas.—Œschner de Coninck.—The ureas were treated with a mixture of neutral potassium chromate and sulphuric acid. In the case of urea, the resulting gas was chiefly CO_2 and a small quantity of nitrogen; sulpho-urea gave sulphocyanic acid as its principal decomposition product, also a residue of ammonium sulphate,—

$$CS\begin{matrix}NH_2\\NH_2\end{matrix} + 4O + 2H_2O = CO_2 + (NH_4)_2SO_4.$$

Phenyl-sulphourea, diphenylsulphourea, methylurea, phenylurea, and diphenylurea gave in each case pure CO_2. Benzylurea gave CO_2 and, amongst other products, a small quantity of benzylcarbimide,—

$$CO\begin{matrix}NH.C_6H_5.CH_2\\NH_2\end{matrix} = NH_3 + CO.N.C_6H_5CH_2.$$

Researches on the Latent Heat of Vaporisation of Piperidine, Pyridine, Acetonitrile, and Capronitrile.—W. Longuinine.—Not suitable for abstraction.

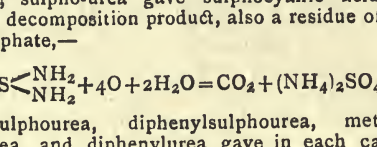
Methyloctenonal.—G. Leser. — The study of the derivatives of this body shows that in certain reactions it has functions under its normal form—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH-CH_2-CH_2-CO-CH_2-CHO;$$

but in other cases it possesses the tautomeric oxymethylene constitution,—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH-CH_2-CH_2-CO-CH=CHOH.$$

Treated with hydroxylamine, an isoxazol was obtained, having the formula—



This is changed into the isomeric nitrile,—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH-CH_2-CH_2-CO-CH_2-CN,$$

by treating in the cold with sodium ethylate, and afterwards adding the calculated quantity of acetic acid. Aniline and methylaniline react with methyloctenonal to give anilides.

———

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 12.

The Limits of Inflammability of Gaseous Mixtures. — H. Le Chatelier and O. Boudouard. — Already inserted.

The Mixed Halogen Salts of Lead.—V. Thomas.—Already inserted in full.

General Reaction of Ethenic Carbides. Corresponding Mercuric Compounds.—Already inserted.

Action of Bromine on Bromide of Ethyl in the presence of Bromide of Aluminium. Preparation of Bromide of Ethylene, (CH_2Br-CH_2Br). — A. Mouneyrat.—Already inserted.

Action of Chloride of Aluminium on Tetrachloride of Acetylene.—A. Mouneyrat.—When these two bodies are heated together to 110° on a paraffin bath a regular disengagement of hydrochloric acid takes place, and the mass becomes darker; when a quantity of hydrochloric acid corresponding to $CCl{\equiv}CCl$ has been collected in the wash bottles, the contents of the flask are thrown into iced water containing a little HCl, the oil after washing and drying is distilled fractionally and two liquids are obtained, one passing over between 130—135° and the other at 147°; the first part is $C_2H_2Cl_4$, and the other is unchanged symmetric tetrachlorethane, $CHCl_2-CHCl_2$.

Action of Bromine on Tetrachloride of Acetylene in the presence of Chloride of Aluminium.—A. Mouneyrat.—188 grms. of tetrachloride of acetylene, 320 grms. of bromine, and 25 grms. of powdered chloride of aluminium, all perfectly dry, are heated in a flask, fitted with a vertical condenser, to 105°, on a paraffin bath, until all the bromine has disappeared; the heavy dark coloured liquid remaining is thrown into distilled water containing a little HCl; after drying it is distilled *in vacuo*, and the greater part of the liquid boils at 140° at a pressure of 7 c.m., and at 194—195° under 76 c.m.: this body has the formula $C_2H_2Cl_2Br_2$, and is therefore dibromodichlorethane.

The Biochemical Preparation of Dioxyacetone (Propanediolone).—G. Bertrand.—Not suitable for abstraction.

Pyrocatechin-ethane and its Derivatives. — Ch. Moureu.—Already inserted.

Heat of Formation of some Quinones with a High Molecular Weight. Thermo-chemistry.—A. Valeur.—Already inserted.

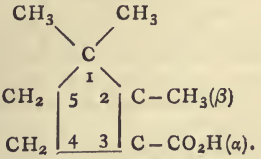
The Quionoximes.—A. Valeur.—Already inserted.

Some Amido-amidines (IV.).—F. Muttelet.—When equal parts of dinitraniline and chloride of benzoyl are heated together on an oil bath, at about 140—150°, a violent effervescence is observed, which continues until fusion is complete, when the temperature will reach 170—180°; the brown product is washed with benzene; the yellow powder thus obtained is only slightly soluble in the ordinary solvents; it is obtained in yellow crystalline grains, melting at 220° with the help of boiling toluene. Analysis shows it to have the formula of a benzoyl derivative, $(NO_2)_2.C_6H_3.NH.CO.C_6H_5$.

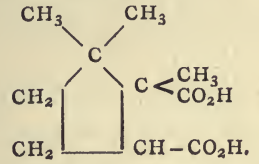
On the Ketones having the Odour of Violets, and on the Compounds of the Citral Series (Geraniol), to which they are Allied.—F. Tiemann.—A very long paper, not suitable for abstraction.

Action of Chlorids of *m*-Nitrated Benzoyl on the Mono-substituted Orthodiamines.—F. Muttelet.—Not suitable for abstraction.

The Constitution of Isolauronolic and Camphoric Acids.—G. Blanc.—The author concludes that the constitution of isolauronolic acid is now fixed with the utmost certainty, and it is dimethyl-1.1 methyl-2-cyclopentene-Δ_2-methyloïc-3 acid.



Camphoric acid is represented thus:—



Absinthine. — P. Bourcet. — Absinthine is a white inodorous body, of extreme and persistent bitterness, crystallising in very fine prismatic needles. It melts at 68°, but traces of impurities lower its melting-point to 65—66°. Absinthine is a glucoside which does not contain any nitrogen; its formula is $C_{15}H_{20}O_4$.

Method of Estimating the Perchlorate in Nitrates of Soda and of Potash.—N. Blattner and J. Brasseur.—Already inserted in full.

Journal de Pharmacie et de Chimie, Series 6, Vol. viii., No. 6.

Volumetric Estimation of the Nitrogen in Urea, or of Urea, by means of an Alkaline Solution of Hypobromite of Soda. — H. Moreigne. — The author describes two methods for this estimation:—1st, after treating the urine with phosphotungstic acid; and 2nd, after treatment with basic acetate of lead and phosphotungstic acid. At first sight the phosphotungstic acid method would appear to be very delicate and require great skill; it is, however, as simple as the well-known basic acetate of lead process, and has this advantage, that it is more accurate. In the second method described the author's idea was to associate the eliminating action of the basic acetate of lead with that of the phosphotungstic reagent. This process, though as simple as the former one from the manipulating point of view, is, however, a little longer, as it requires two precipitations and two filtrations.

Estimation of Sugar in Chocolate. — P. Carles.— 16·20 grms. of powdered chocolate are placed in a 100 c.c. flask with about 80 c.c. of water, and boiled on the water-bath for half an hour; 2 or 3 c.c. of a solution of subacetate of lead are then added, the contents are well shaken, and made up to 100 c.c. Cool and filter. The colourless liquor is examined in the saccharimeter, and the reading N found is modified by the following formula, which gives the result sought for:—

$$N-\frac{N\times 8{\cdot}10}{100}=x.$$

On a Chloro-iodide of Tin.—C. Lenormand.—Already inserted in full.

Vol. viii., Nos. 7 and 8.

These two numbers contain no matter of chemical interest.

Vol. viii., No. 9.

The Volumetric Estimation of Ethylic Aldehyde. —M. Rocques.—In devising a new method for the estimation of ethylic aldehyde the author has made use of three quantitative reactions of aldehyde:—1. The action of sulphurous acid on bisulphites; 2. The action of nitrate of silver in the presence of ammonia and caustic soda; and 3. The action of hypochlorites. The first method gave the best and most concordant result. The method of working was as follows:—Two solutions, S and I, were prepared, the first by dissolving 12 6 grms. of pure sulphite of soda in 400 c.c. of water, adding 100 c.c. of sulphuric acid, and making the volume up to 1 litre with pure alcohol at 96°. This is filtered on the following day. The second solution is a normal solution of iodine in iodide of potassium; 1 c.c. corresponds to 0·0032 grm. of sulphurous acid and to 0·0022 grm. of ethylic aldehyde. The solution S is titrated by means of the solution I in the presence of starch; 10 c.c. of S should require 20 c.c. of I. To estimate the aldehyde in an alcoholic solution we place 10 c.c. in a 100 c.c. flask, add 50 c.c. of S, and make up to 100 c.c. with pure alcohol at 50°; in another flask we put 50 c.c. of S, and make up to 100 c.c. with pure alcohol at 50°; both flasks must be well shaken. On the following day take 50 c.c. of each and titrate the free sulphurous acid with solution I, adding about 50 c.c. of water and a little starch. If A is the number of cubic centimetres of solution I required by the check solution, and *a* the number required by the solution containing the aldehyde, the proportion of aldehyde present per litre will be $(A-a)\times 0{\cdot}0022\times 200$. If the solution contains less than 1 per cent of aldehyde the solutions S and I must be diluted.

Vol. viii., No. 10.

This number contains no matter of chemical interest.

Vol. viii., No. 11.

Digitalic Ferment.—MM. Brissemoret and Joanne.— In 1875 Kosmann prepared a nitrated substance from the leaves of purple digitalis, which he regarded as a hydrating ferment. Acco ding to him this ferment had the properties of diastase; it transforms, by hydration, cane-sugar into glucose, starch into dextrine, and salicine into glucose and saligenine. The authors find that it possesses oxidising properties, has great analogies with the oxidases isolated by Bertrand from a large number of vegetable phanerogams, and is not destroyed by desiccation.

The Volumetric Estimation of Ethylic Alcohol.— X. Rocques.—Further experiments on the estimation of ethylic alcohol by the action of alkaline bisulphites on this body show that temperature exercises a considerable influence on the reaction, and, while the reaction is complete in less than twenty-four hours at 25° to 30°, it is not finished after forty-eight hours when the temperature is lowered to 15°.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—W. B. Bannerman, A. Bellin, Lady Currie, C. H. Gatty, A. C. Gibbons, E. J. Gibbons, Mrs. Horne, Mrs. Kraftmeier, Sir G. H. Lewis, Mrs. J. List, F. J. Longton, O. S. Macleay, Mrs. Parker, H. Pulford, and Colonel E. Sartorius, V.C., C.B. The special thanks of the Members were returned to Sir Andrew Noble, K.C.B., for his donation of £100, and to Mr. Edward Kraftmeier for his donation of £52 10s. to the fund for the promotion of Experimental Research at Low Temperatures. His Grace the Duke of Northumberland

was elected President of the Royal Institution in the place of the late Duke, his father.

Water Supplies and the Fever Death-rate.—In a letter to a provincial contemporary, Mr. A. H. Smee gives some very interesting figures bearing on the fever death-rate and the water supplies of various large towns, both in Great Britain and on the Continent. Out of twenty-two towns in Great Britain it is very satisfactory to note that London, the *only one* supplied with river water, is almost the best, the fever death-rate being only 67 per million; Brighton 66, Bristol 56, and Plymouth 40, being the only towns to beat it, whereas the much vaunted supplies of Glasgow, Liverpool, and Manchester give fever death-rates of 184, 172, and 133 respectively. Belfast is the worst, with 1667 per million.

A Table for the Restoration of Weak Sulphuric Acid to Acid of 98 per cent H_2SO_4. — This useful table, calculated and checked by Messrs. R. Friswell, F.I.C., T. Lawson, F.I.C., and F. Evershed, F.C.S., and published by Messrs. Brooke, Simpson, and Spiller, Ltd., shows at a glance the number of lbs. of "oleum" containing 60 per cent SO_3 and 40 per cent H_2SO_4 to be added to 1000 lbs. of weak acid of specific gravities varying from 1·7 to 1·8 in order to bring it up to the strength 98 per cent H_2SO_4. The table is available for pure dilute sulphuric acid by a determination of the specific gravity, and in other cases by a determination of the sulphuric acid, calculated either as SO_3 or H_2SO_4.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Society of Arts, 8 (Cantor Lectures). "Cycle Construction and Design," by Archibald Sharpe, A.M.Inst.C.E.

TUESDAY, 14th.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.

WEDNESDAY, 15th.—Society of Arts, 8. "Liquid Fuel," by Sir Marcus Samuel.

—— Microscopical, 8. "The Projection Microscope," by Lewis Wright.

—— Institution of Mining and Metallurgy, 8. "On Crushing and Concentration at Dolcoath Mine, Cornwall," by R. Arthur Thomas, M.Inst.M.M. "On Charcoal Precipitation from Auro-Cyanide Solutions," by John I. Lowles, M.Inst.M.M. "Notes on the Electro-Deposition of Vanadium," by Sherard Cowper-Coles, M.Inst.M.M.

THURSDAY, 16th.—Royal Institution, 3. "English Playhouses in the Sixteenth, Seventeenth, and Eighteenth Centuries," by Willian Poel.

—— Chemical, 8. "Influence of Substitution on Specific Rotation on the Bornylamine Series," by H. O. Forster, Ph.D. "Rotatory Power of Optically Active Methoxy- and Ethoxy-Propionic Acids prepared from Active Lactic Acid," by Thomas Purdie, F.R.S., and James C. Irvine, B.Sc.

FRIDAY, 10th.—Royal Institution, 9. "The Electric Fish of the Nile," by Prof. Francis Gotch, F.R.S.

SATURDAY, 18th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

TECHNOLOGICAL EXAMINATIONS, 1899.
CITY AND GUILDS OF LONDON INSTITUTE.

The Institute's Examinations in Technology will be held on April 26th, 29th, May 1st, 2nd, 3rd, 4th, 6th, 8th, 9th, 12th, 13th, June 3rd and 10th.

All applications from Local Secretaries for examination in Technology must be forwarded to the Institute on or before March 20th.

Only in exceptional cases, and by payment of an additional fee, can applications be received from Local Secretaries after that date.

Candidates in Technology not attending any registered class should apply at once to the Secretary of the nearest Local Centre.

Applications from any individual candidates for examination at the Offices of the Institute should be made not later than March 30th, addressed to the Examinations Department, City and Guilds of London Institute, Exhibition Road, London, S.W., and should be accompanied by a Postal Order for the amount of the fee—the Subject and Grade of Examination being clearly stated.

By Order of the Directors, who are transferring their business to their other Works.

TO CHEMICAL AND MANURE MANUFACTURERS, ENGINEERS, MACHINERY USERS, AND OTHERS.

VICTORIA DOCKS.—Sale of the remaining Plant and Machinery, situate at Messrs. James Gibbs and Co.'s, Upper Works, North Woolwich Road.

MESSRS. GREEN and SON are instructed by the Directors to SELL by AUCTION, in Lots, on the Premises, Upper Works, North Woolwich Road, on MONDAY, MARCH 20, 1899, at Twelve for One o'clock precisely, the remaining CHEMICAL PLANT, Machinery, and other matters belonging to Messrs. James Gibbs and Co. (Limited), and comprising manure plant, alum cake plant, including wrought iron calcining cylinder, 54 ft. long, with furnace; phosphate mill plant, including eight pairs of 4 ft. 6 in. mill stones, complete with gear, Blake Marsden stone crusher, four Mumford and Moodie's separators; the acid plant, comprising two sets of pyrites kilns, with 56 furnace fronts, fitted complete, with doors, bars, &c., acid eggs, &c.; the steam power includes a splendid 200 h.p. steam engine, with high and low pressure cylinders and eight C.I surface condensers by Simpson and Co., a double cylinder tandem air compressor, and two small engines, six Cornish boilers, 6 ft. dia. by 28 ft. long, about 500 ft. of shafting, with pulleys, riggers, and belting; two three-ton cranes, four-ton weighbridge, and two three-ton ditto; about 1000 ft. of tram lines, and about 300 iron columns each 18 ft. to 20 ft long, forge, sundry utensils, tools, two useful vans, office furniture, &c.

NOTE. The Freehold Property, covering an area of over three acres, with frontage of 100 ft. to the river, and comprising useful buildings, is for sale by private contract.

May be viewed on the Friday and Saturday prior to the Sale.

Catalogues of Messrs. LINKLATER, ADDISON, BROWN, and JONES, Solicitors, 2, Bond Court, Walbrook, E.C.; on the Premises; and of Messrs. GREEN and SON, Auctioneers and Surveyors, 28 and 29, St. Swithin's Lane, E.C.

TO MANUFACTURERS AND OTHERS REQUIRING STEAM POWER.

By Order of the Directors of JAMES GIBBS and CO. (Limited).—Sale of Remaining Plant and Machinery at VICTORIA DOCK,

MESSRS. GREEN and SON desire to draw particular attention of purchasers of machinery to Lot 118 at their Sale on Monday, March 20, as noticed above. It comprises a splendid 200 h.p. COMPOUND CONDENSING STEAM ENGINE by Simpsons, of Pimlico. It has been in working order for several years, and shows particularly satisfactory working; it is most compact and in thorough order, the whole being well set and standing on brick and stone foundations. The average pressure of 60 lb. and 45 revolutions gives the indicated h.p. as mentioned above, and, with slightly increased pressure, can easily work to 300 h.p.

Catalogues of Messrs. GREEN and SON, Auctioneers and Surveyors, 28 and 29, St. Swithin's Lane, E.C,

TO MANUFACTURING AND BUSINESS FIRMS.

TO BE SOLD.

FREEHOLD LONDON PROPERTIES, offering good opportunities for a large firm requiring a branch establishment in London.

I.—Freehold property, area three acres, frontage of 190 feet to the River Thames. Good depth of water, and covered with buildings suitable for many purposes.

II.—Freehold Property, within 2½ miles of the City. Waterside frontage of 290 feet, and some very substantial buildings, with room for extension.

III.—Compact Manufacturing Premises. Waterside frontage of 154 feet, area 31,000 square feet, substantial buildings, and fitted with steam power.

Particulars of the above may be obtained from Messrs. GREEN and SON, Auctioneers and Surveyors, 28 and 29, St. Swithin's Lane, London, E.C.

THE YORKSHIRE COLLEGE, LEEDS.

DEPARTMENT OF LEATHER INDUSTRIES.

Applications will be received up to March 16th for the Appointment of ASSISTANT LECTURER and DEMONSTRATOR in LEATHER INDUSTRIES. A sound training in Chemistry is essential; Technical Knowledge, although desirable, is not indispensable. Salary to commence at £150 a year.—Further particulars may be obtained from the SECRETARY of the College.

FOR SALE.—Chemical Balance by Oertling. Perfect condition, good as new, cost 18 guineas.—For particulars apply to "Analyst," care of Mr. Wilson, Chemist, Ordnance Road, Enfield Lock, London, N.

LABORATORY TO BE LET.—Centrally situated. Very moderate rental.—Address, "Laboratory," care of Housekeeper, 34, Old Broad Street, E.C.

THE CHEMICAL NEWS.

Vol. LXXIX., No. 2051.

ON HYDROGEN PEROXIDE AS THE ACTIVE AGENT IN PRODUCING PICTURES ON A PHOTOGRAPHIC PLATE IN THE DARK.*

By W. J. RUSSELL, Ph.D., V.P.R.S.

In previous papers it has been shown that certain bodies are able, in the dark, to act on a photographic plate and produce a picture. The purpose of the present communication is to show that in all the cases which have been examined, and probably in all others of a similar kind, the action which occurs is due to the presence of hydrogen peroxide. As a sensitive plate always contains moisture, and probably would be inactive if quite dry, it does not seem possible to test the truth of this statement by the total exclusion of moisture; therefore more indirect means have to be adopted. In the following paper no attempt is made to explain the reactions which occur in the plate itself; that is a distinct question, and at present the object is to consider the means by which these changes, whatever they may be, are brought about. These changes are rendered visible by exactly the same processes as those adopted for the development of an ordinary light picture. Any of the ordinary photographic plates may be used in these experiments, but as many of the pictures are only formed after a long exposure it is well to use rapid plates. In the following experiments the plate used has been in almost all cases the "Ilford special rapid," and the process of development has in every case been that recommended for their ordinary use.

The first step towards demonstrating that hydrogen peroxide is the active agent in producing these pictures, is to show that all the results produced both by metals and by organic bodies on a photographic plate can be produced by hydrogen peroxide. This body is now made in considerable quantities and sold in aqueous solution of a given strength. This commercial article appears to act equally well to a carefully prepared and pure specimen of the same strength.

A convenient way of testing the action of any liquid on a photographic plate is to use a small circular glass dish, such as is made for bacteriological experiments, the photographic plate resting on the top of the dish, and the amount of the liquid used determines the distance the plate is from the active surface, the experiment being carried on in complete darkness. If pure water be tested in this way, it is found that no picture, that is no darkening of the plate, occurs on its being treated with the developing solution. The plate can be left over the water for eighteen to twenty hours, but if left longer than this the film is destroyed by the aqueous vapour. If to the pure water in the dish a mere trace of hydrogen peroxide be added, a darkening of the plate will quickly occur. For instance, if the liquid contains only one part of the peroxide in a million of water, and the plate be exposed to its action for eighteen hours, a faint picture is produced. Bearing in mind the small amount of evaporation which takes place under these conditions, and consequently the minute amount of the peroxide which comes in contact with the plate, it clearly shows the exceeding delicacy of the reaction.

Again, if a piece of Ford blotting-paper, which by itself is inactive, be wetted with a solution of one part of peroxide in 500,000 of water, and be hung up in a warm room for three-quarters of an hour to dry, and placed in contact with a photographic plate for two hours at a temperature of 55° C., on subjecting the plate to development a distinct picture is produced. In fact, moistening good blotting-paper with a solution which may be strong or weak, and allowing it to dry for a long or short time, is a very good way of applying the peroxide. In place of blotting-paper any inactive porous substance may be used.

Plaster of Paris wetted with a peroxide solution and allowed to set, continues for a long time to be an active body. If by any of these means a large, in place of a small, amount of the peroxide be allowed to act on a plate, then in place of a dark, a light picture is obtained, a phenomenon similar to what is known to photographers as reversal.

The conditions under which certain metals and certain organic bodies act on photographic plates, and how pictures of the structure of paper, skeleton leaves, lace, and other bodies can be obtained, has already been described, so that now it is only necessary to say that substitute for these active bodies peroxide of hydrogen, and exactly corresponding results are produced. Writing with ordinary ink, or with a solution of ferrous sulphate, or potassium ferrocyanide, has been shown to be opaque to the action of zinc and of turpentine, so is it to the action of the peroxide of hydrogen. Further, the action exerted by the metals and the terpenes is unable to pass through glass, mica, selenite, &c., but is able to pass through thin sheets of gelatin, celluloid, guttapercha, indiarubber, tracing-paper, gold-beaters' skin, parchment, &c.; peroxide of hydrogen acts exactly in the same way, every body which is known to be either opaque or transparent to the action of the metals or terpenes is opaque or transpareni to the action of the peroxide; so that, as far as the production of similar phenomena goes, the agreement is complete. Of the acknowledged tests for the preeence of hydrogen peroxide, the one with the titanic acid dissolved in sulphuric acid is exceedingly delicate; so also appears to be the tetramethylparaphenylenediamine paper of Dr. Wurster, and both of them have been made use of.

The next point which naturally suggests itself is, whether peroxide of hydrogen is, or is likely to be, present in all the different cases, when action on the sensitive plate occurs. First, with regard to the metals. The list of the active metals, which has already been given, is as follows, arranged approximately in order of their activity:—Magnesium, cadmium, zinc, nickel, aluminium, lead, cobalt, bismuth, tin. Now these are certainly the metals which might be expected to decompose water, and in the presence of oxygen cause the formation of hydrogen peroxide, and still more the order in which they stand in the above list, judging from their general properties, is that in which they would probably induce the formation of the peroxide. It is also satisfactory to note that this list of metals and their order of activity was drawn up simply from experiment, when there was no idea that hydrogen peroxide had anything to do with the reaction. Again, as a confirmation that hydrogen peroxide is formed when these metals oxidise in moist air, pieces of Dr. Wurster's tetra-paper were moistened and laid on bright surfaces of the metal. With the metals that head the foregoing list a considerable amount of blue colour was rapidly developed; with the metals at the end of the list the amount of colour was less, and the reaction slower; and with other metals, such as silver and platinum, there was no action. With copper and with iron a very slight amount of action did occur, but these metals do not appear able to produce definite pictures. Iodide of potassium and starch paper, where used in the same way, gave a blue colour with all the active metals, but none with copper nor with iron.

On the supposition that hydrogen peroxide is the active agent in the action exerted by the metals, it seemed probable that on supplying to the metal more moisture than it obtained from the air and photographic plate, more action would take place, and this was found to be the case. Two pieces of polished zinc were placed in contact with photographic plates in small iron boxes; one box was

* A Paper read before the Royal Society, March 2, 1899.

quite dry, and put in a bell jar over calcium chloride, and into the other box some damp paper was introduced, and the box was placed with a little water under a bell jar. On examining the plates after three days it was found that the damp plate had much the darker picture on it.

With the object of obtaining an increased amount of action, experiments were made by passing a current of warm moist air over zinc turnings. A glass tube, 6 feet long and 1 inch in diameter, was packed with zinc turnings and placed within a large brass tube to which steam could be admitted. The amount of action, if any, was indicated on a plate, placed in a dark box at the end of the tube. Even under the most favourable conditions no very large amount of action took place. When a current of moist warm air was passed through the tube for an hour a fairly dark picture was obtained. If the air was dry no picture appeared. If amalgamated zinc was used in place of pure zinc a darker picture was formed, and, as a check on these results, dry and moist air, both warm and at ordinary temperatures, was passed through the tube, no zinc being present, and then no action took place. Also when ozonised air was passed through the tube there was no action. Passing now from the metals to the organic bodies capable of acting on a photographic plate, it has been found that they belong essentially, if not solely, to that class of bodies known as terpenes, and it is a general property of all this class of bodies when oxidising to give rise to hydrogen peroxide. Thanks to Dr. Tilden, experiments have been made with most of the terpenes, and all were found to be very active bodies; both pinene and limonene were tried, in their dextro- and lævo-rotatory state, but their activity appeared to be the same. Oxidised and other compounds connected with the terpenes, such as terpineol camphor, thymol cymene, have no power of acting on a photographic plate, but ordinary turpentine and terebene are very active bodies.

Most of the ordinary essential oils, such as bergamot, peppermint, pine, lemons, cajuput, &c., have been experimented with, and, without exception, have been found to be active bodies. It is well known that they all contain terpenes; they are also characterised by a strong odour, and as ordinary scents contain some of these bodies, it follows that almost all vegetable bodies having a strong smell are capable of acting on a photographic plate. Eau de Cologne gives a good picture, so do many wines and brandy, and coffee, guiacum, cinnamon are also active substances; thus the photographic plate becomes a very delicate test for the presence of all these bodies, and as the action is cumulative it may even compete with the sense of smell.

In addition to the essential oils, the ordinary vegetable oils, such as linseed oil, which is the most active, and colza and olive, which are much less active and have much less power of absorbing oxygen from the air, can act on a photographic plate. The tetra-paper readily goes blue if suspended in a bell jar which has a few drops of linseed oil in a dish within it.

The mineral oils are, on the contrary, devoid of this power of acting on the sensitive plate, and the same applies to bodies such as benzene, phenol, naphthalene, aldehyde, methyl alcohol, coal naphtha, &c.

It would seem, then, that all the organic bodies capable of acting on the photographic plate are capable of giving rise to the formation of hydrogen peroxide when they oxidise in moist air.

(To be continued).

On 2-Oxydibenzalacetone.—St. v. Kostanecki and D. Maron.—The results are here given which were obtained with some colouring-matters containing chromophore, $C=C.CO.C=C$, a compound with the same members arranged in a different order. These compounds take rise from the action of aldehyds on an unsaturated ketone, $R.CH=CH.CO.CH_3$, prepared from acetone. Among the aldehyds, benzaldehyd, furfurol, and piperonal have been used.—*Ber. Deutsch. Chem. Gesell.*

A CONTRIBUTION TO AGRICULTURAL CHEMISTRY: CARDAMOMS.

By H. B. YARDLEY.

HAVING made search in likely publications, I can find no analyses of the ash of *Cardamoms*, either plant or seed; it may therefore be interesting to others and desirable to place on record the annexed analysis of some of the seeds (and husks) performed in my laboratory lately:—

The mineral matters (ash) amounted to 4·19 per cent. It was of a grey colour, probably due to a small quantity of carbon which it was found impossible to entirely burn off. This ash gave:—

Lime	13·33
Oxide of iron	0·51
Alumina	1·53
Magnesia	4·52
Soda	20·43
Potash	10·42
Phosphoric anhydride	6·00*
Sulphuric anhydride	12 66
Chlorine	2·54
Silica	24·81
Carbonic anhydride, carbon, &c.	4·40
	101·15
Less oxygen = chlorine	1·15
	100·00

* Equal to tribasic phosphate of lime.

The organic constitution of the seeds was not required, and there are already published records.

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London, N.E.

THE SEPARATION AND ESTIMATION OF LEAD BY ELECTRICAL MEANS IN ITS PRINCIPAL ALLOYS AND IN COMMERCIAL METALS.

By A. HOLLARD.

THE estimation of lead by electrical means in the state of binoxide is of incomparable exactness and simplicity, provided that a certain number of precautions are observed very closely, such as density of current, composition of the electrolyte, temperature of desiccation of the deposit of binoxide of lead, &c. These data have up to the present been incomplete, and the results sometimes incorrect; we believe we have now elaborated and defined them in a strict manner. We have also laid down the conditions under which the method may be applied to the most widely divergent alloys. It is only after experiments carried out under the most varying conditions and methods of control, during the course of several years, that we publish this method, believing that it will be found to be of great service.

The deposits of binoxide of lead which occur exclusively on the anode are *very adherent*, and correspond exactly to the formula PbO_2; further, no trace of metallic lead is deposited on the cathode.

The quantity of lead submitted to estimation need not be more than 0·2 grm.; with a larger quantity, in fact, there is a danger of the deposit not being sufficiently adherent.

Electrolytic Apparatus.—Our electrodes consist of a truncated cone of platinum which serves as anode, and on which the binoxide of lead is deposited; the cathode is a spiral of platinum wire fixed on a stand. They are, in fact, Lukow's apparatus modified as to construction

and dimensions; the truncated cone is made of a sheet of pure platinum, its upper diameter is 18 m.m. and its lower diameter 45 m.m., its generatrix 63 m.m. A hard platinum wire is gold-soldered to the trunk of the cone. Each electrode weighs about 20 grms.

The vessels containing the electrolytes are of ordinary cylindrical Bohemian glass, about 6·5 c.m. diameter, holding about 370 to 400 c.c. The solution of the alloy, as well as the electrolysis of the lead, is conducted in the same beaker; the whole operation does not require, as will be seen, either decantation or filtration. During the attack with acid the beaker must be covered with a funnel, the edge of which should rest just inside the edge of the beaker, forming a little gutter in which a few drops of water will make a perfect hydraulic joint; all loss by projection is thus avoided. The distance from the lower edge of the cone to the foot of the spiral should be about 6 m.m. For better receiving the electrolytic deposit of lead the cone should not be polished, but dull, so that the deposit will adhere to it more easily. This can be effected by immersing the platinum in aqua regia for a few hours.

I. *Estimation of Pure Lead.*

The lead is dissolved in dilute nitric acid. The solution, diluted to about 350 c.c., should contain 80 c.c. of ordinary pure nitric acid in the free state. With a less quantity of acid there is a liability to deposit part of the lead on the cathode. The electrolysis is effected at the ordinary temperature with a current of 0·15 ampère. The voltage cannot be defined; it depends on the quantity of lead in the electrolyte, and, in the case of alloys, on the nature and proportion of foreign metals present.*

The cone should be plunged completely into the bath, and the foot of the spiral should be as near as possible to the bottom of the beaker. The electrolysis goes on at the ordinary temperature. At the end of twenty-four hours the precipitation is complete and the deposit very adherent. The cone is then plunged successively into two beakers filled with distilled water, and then placed in an oven and heated gradually to 200°, which temperature should be maintained for a quarter of an hour. *This temperature is absolutely necessary to obtain a deposit corresponding exactly with the formula* PbO_2.

II. *Separation and Estimation of Lead in Commercial Zinc.*

Ten or twenty grms. of zinc, according to the purity of the metal, are dissolved in such a quantity of dilute nitric acid that when the solution is effected, 80 c.c. of ordinary pure nitric acid remain in the free state (1 grm. of zinc in dissolving combines with 3·5 c.c. of ordinary pure acid. The rest of the operation is carried out as described above.

The lead once separated, the other impurities in the zinc can be estimated very easily, and much more easily than by the ordinary method. The estimation of cadmium in particular, so difficult by the ordinary method, becomes very simple; the whole of this metal is, in fact, found in the bath, free from lead; it suffices to evaporate down this solution, in presence of sulphuric acid, to drive off the nitric acid, and then precipitate the cadmium by means of sulphuretted hydrogen in the ordinary way.

III. *Separation and Estimation of Lead in Alloys of Lead and Tin, and in Commercial Tin.*

1. *An Alloy containing more than 4 per cent of Lead.*—Proceed as described above (Part I.), taking note in the determination of the amount of free acid present that 1 grm. of tin decomposes while dissolving 2 c.c. of ordinary pure nitric acid. The alloy should be in the form of fine turnings, or, better still, filings. The precipitated oxide of tin should not be filtered; it should simply be collected together at the bottom of the beaker in the following manner:—The solution, diluted to about 350 c.c., should be heated to 90° until the oxide of tin collects at the bottom; the flame is then taken away, when the deposit remains compact on cooling.

2. *Alloys containing less than 4 per cent of Lead.*—These alloys contain a large proportion of tin in comparison with the amount of lead present, and their solutions should be electrolysed in very large beakers. Under these conditions the oxide of tin forms a thin layer at the bottom of the beaker; there is then no risk of carrying off lead from the solution, or even of retaining small particles of unattacked alloy, and thus losing a part of the metal under analysis. The beakers, which will serve both for the solution of the alloy and electrolysis, should be 10·5 c.m. in diameter with a capacity of about 1 litre. The solution should be effected warm on 5 grms. of the alloy, with dilute nitric acid containing 260 c.c. of ordinary pure acid. The solution should then be diluted to about 650 c.c.; the oxide of tin is then collected at the bottom of the beaker as described above.

3. *Commercial Tin.*—This should be treated in exactly the same manner as alloys containing less than 4 per cent of lead (2).

IV. *Separation and Estimation of Lead in Alloys of Lead and Antimony, and in Commercial Antimony.*

As the deposits of binoxide of lead carry with them oxide of antimony, the method we have described for tin and its alloys is not applicable. This oxide of antimony comes from the antimony dissolved in the solution.

V. *Separation and Estimation of Lead in Commercial Copper and its Alloys (Brasses and Bronzes).*

In the presence of a certain amount of copper, the integral separation of lead in the state of binoxide requires a much smaller quantity of nitric acid and a stronger current than in the preceding cases. We shall give the reason for this later on.

We take a quantity of the alloy, or of copper containing at least 1 grm. of this metal, and we attack it with dilute nitric acid in sufficient quantity to leave an excess of 14 c.c. of ordinary pure nitric acid after solution; 1 grm. of copper in dissolving combines with 3·6 c.c. of this acid. The solution is diluted to 350 c.c. The intensity of the current should be 0·3 ampère, and the duration of the electrolysis about eighteen hours.

When lead is present in the copper or its alloys, as an impurity only, we take 10 grms. of the metal, as has already been pointed out in the analysis of the impurities of commercial copper (A. Hollard, *Comptes Rendus*, cxxiii., p. 1065), bronzes and brasses (A. Hollard, *Bull. Soc. Chim.*, 1897, Series 3, xvii., 886).

Reactions produced in the course of the preceding Analytical Operations.—From what has preceded it will be seen that the density of the current and the proportion of the free nitric acid necessary for the electrolytic separation of the lead in the state of binoxide, vary according to whether we have to deal with an alloy of copper or an alloy not containing this metal. We can easily see the reason for this difference by the following considerations:—In all the metals or alloys that we have experimented with, the lead has been brought to the state of nitrate, and we know that the normal electrolysis of this nitrate gives rise to the reaction—

$$(NO_3)_2Pb = \underbrace{N_2O_3 + O}_{\text{On the anode.}} + \underbrace{Pb}_{\text{On the cathode.}}$$

The deposit of lead in the state of binoxide (PbO_2) on the anode necessitates a supplementary supply of oxygen. In the case of an alloy not containing copper, this oxygen comes entirely from the electrolysis of the free nitric acid, $2NO_3H = N_2O_5 + O + H$. In the case of alloys of copper this oxygen comes on the one hand from the electrolysis of the nitrate of copper, $(NO_3)_2Cu = N_2O_5 + O + Cu$, and on the other hand from the electrolysis of the free nitric

* For 0·2 grm. of pure lead under the conditions described above the electromotive force should be from 2·6 to 2·7 volts.

acid. We can easily see that in such a case the quantity of this acid present can be considerably diminished.

As to the difference of the density of the current, this is explained by the fact that the products separated at the cathode and the electrolytic reactions are very different in the presence and in the absence of copper.—*Bull. Soc. Chim.*, Series 3, vol. xiv. xv., No. 22.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 2nd, 1899.

Professor Dewar, F.R.S., President, in the Chair.

Mr. John S. MacArthur was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Clement Harrison Baker, Athelney, Featherstone Road, King's Heath, Birmingham; Frederick James Beale, Wilderspool Brewery, Warrington; Alfred Ernest Bond, Prince's Chambers, Corporation Street, Birmingham; Charles Robert Darling, 220, Eglinton Road, Plumstead; Percy Haigh, 312, Romford Road, Forest Gate, E.; Thomas Judge, 142, Waller Road, New Cross, S.E.; William McConnell, 178, Springfield Road, Glasgow; Wilfred Walter Morris, Newtown St. Boswells, Roxburghshire, N.B.; Maurice Emile Schweich, 85, Belgrave Road, S.W.; Edward Thomas Shelbourn, 1, Chalcot Crescent, Regent's Park Road, N.W.; Richard Threlfall, 45, Frederick Road, Edgbaston, Birmingham; Ernest Albert Tyler, Warsop, Mansfield, Notts.

Of the following papers those marked * were read:—

*35. "*Bromomethylfurfuraldehyde.*" By H. J. H. Fenton, M.A., and Mildred Gostling, B.Sc.

It has been shown by the authors in a previous communication (*Trans.*, 1898, lxxiii., 556) that certain carbohydrates, when acted on by hydrogen bromide in ethereal solution, give rise to a beautiful purple colouration. From observations made with a considerable number of typical carbohydrates, it would appear that the rapid production of this intense colour is characteristic of ketohexoses, or substances capable of yielding them by hydrolysis. The colour-producing substance has now been isolated in a pure state, and is obtained in the form of short, golden-yellow, prismatic crystals belonging to the oblique system. It melts at 60°, decomposes somewhat explosively at a higher temperature, and is practically insoluble in cold water, but dissolves easily in most organic solvents, giving solutions which powerfully stain the skin. Its solutions give a bright orange colour with aniline acetate after some time; they powerfully reduce silver and copper solutions, react with phenylhydrazine, and when treated with an ethereal solution of hydrogen bromide produce an intense purple colouration, which is exactly similar to, but appears even more quickly than, that obtained with ketohexoses. Analysis and molecular weight determinations show that it has the formula $C_6H_5BrO_2$, and its reactions and properties indicate that it is a bromomethylfurfuraldehyde,—

$$\begin{array}{l} H\cdot C{=}C-CHO \\ \quad\ |\ \ |{>}O \\ H\cdot C{=}C-CH_2Br \end{array},$$

On oxidation with silver oxide it yields ω-hydroxymethylpyromucic acid, identical with that obtained by Hill and Jennings from the corresponding bromo-acid (*Amer. Chem. Journ.*, 1893, xv., 162). The whole of the bromine is precipitated by an alcoholic solution of silver nitrate, and from the solution a substance is obtained which closely resembles, but seems to be isomeric with, the hydroxymethylfurfuraldehyde of Düll and Kiermayer (*Chem. Zeit.*, 1895, xix., 206, 1003); a similar result is obtained by heating the substance with water in presence of barium carbonate. If the substance be covered with water and saturated with sulphur dioxide, it slowly dissolves, and the solution, after remaining for some hours, gives, on extraction by ether, a product which crystallises from hot water in yellow needles; these melt at 117°, and in solution give a magnificent blue colour with caustic alkalis. Analysis and molecular weight determinations indicate that this is a condensation product, and is free from bromine; its constitution is now being investigated.

*36. "*The Reaction of Alkyl Iodides with Hydroxylamine. Formation of Alkylated Hydroxylamines and Oxamines.*" By Wyndham R. Dunstan, F.R.S., and Ernest Goulding, B.Sc.

As the authors have shown previously (*Proc.*, 1894, x., 138; *Trans.*, 1896, lxix., 839), methyl iodide readily reacts with hydroxylamine, forming hydriodides of hydroxylamine and the hydriodide of a trimethyl derivative. The hydrated base crystallises well, and melts sharply at 96°. It is not volatile. The anhydrous base has not yet been isolated. The aqueous solution is strongly alkaline, and does not reduce Fehling's solution. Solution of silver nitrate is only reduced on warming, or after prolonged standing. Dimethylamine and formaldehyde are produced by the action of hydriodic acid, but no methyl iodide. The same decomposition ensues when the base (or its salts) is heated either alone or with dilute sulphuric acid, $(CH_3)_3NO=CH_2O+NH(CH_3)_2$. When allowed to stand in aqueous solution in contact with zinc dust, it is reduced to trimethylamine, $(CH_3)_3NO+H_2=(CH_3)_3N+H_2O$.

The principal salts of the base are described.

The authors conclude that this substance is not a true trimethylhydroxylamine, but a *trimethyloxyammonia* or *trimethyloxamine*, $(CH_3)_3N{:}O$.

By the reaction of methyl iodide with trimethyloxamine the iodide of a tetramethyl derivative is produced. The free base, which is strongly alkaline, has, so far, been obtained only in aqueous solution. The salts crystallise well.

When the solution of a salt is warmed with an alkali, methyl alcohol is split off and trimethyloxamine is formed, $N(CH_3)_3OCH_3OH=N(CH_3)_3O+CH_3OH$.

When the aqueous solution of a salt is heated at 150 in a closed tube, trimethylamine and formaldehyde are produced, $N(CH_3)_3OCH_3OH=N(CH_3)_3+CH_2O+H_2O$.

When the iodide is heated with concentrated hydriodic acid, the products are methyl iodide, dimethylamine, and formaldehyde,—

$$N(CH_3)_3OCH_3OH+HI=$$
$$=NH(CH_3)_2+CH_3I+CH_2O+H_2O.$$

When reduced in aqueous solution with zinc dust, trimethylamine and methyl alcohol are formed,—

$$N(CH_3)_3OCH_3OH+H_2=N(CH_3)_3+CH_3OH+H_2O.$$

The base is, therefore, *trimethylmethoxyammonium hydroxide*, $(CH_3)_3N{\cdot}OCH_3{\cdot}OH$.

When ethyl iodide reacts with hydroxylamine, hydriodides of hydrozylamine are formed, together with a *diethylhydroxylamine hydriodide*. The base is an oily liquid with a curious aromatic odour, boiling, with some decomposition, between 130—134°. Its aqueous solution is strongly alkaline, and acts as a powerful reducing agent. The salts are fully described; the oxalate, $[(C_2H_5)_2NOH]_2H_2C_2O_4$, crystallises very readily and melts at 136—137°. When heated it decomposes into ethylamine and acetaldehyde,—

$$(C_2H_5)_2NOH=C_2H_5NH_2+C_2H_4O.$$

When heated with hydriodic acid, diethylamine is formed, but no ethyl iodide. It forms an acetyl derivative. The substance is, therefore, a true *β-diethylhydroxylamine*, $N(C_2H_5)_2OH$. It is isomeric with the two diethylhydroxylamines described by Lossen (NHEtOEt), but is probably identical with the substance obtained by Kissel

by the action of zinc ethyl on nitroethane. The substance now described closely resembles in its decompositions the β-dibenzylhydroxylamine studied by Behrend and Leuchs.

By the reaction of diethylhydroxylamine with ethyl iodide, the hydriodide of a triethyl derivative is obtained. The base is crystalline and non-volatile. The aqueous solution is strongly alkaline. It does not reduce Fehling's solution, but reduces silver nitrate on warming. The principal salts are fully described. In all its reactions this base closely corresponds with trimethyloxamine. When heated it breaks up into diethylamine and acetaldehyde; when reduced with zinc dust in aqueous solution it furnishes triethylamine, whilst by the action of hydriodic acid it is converted into triethylamine without the formation of ethyl iodide. This substance is, therefore, *triethyloxyammonia* or *triethyloxamine*, $(C_2H_5)_3N{:}O$. It is not identical with the isomeride of triethylhydroxylamine which Bewad describes as resulting from the action of zinc ethyl on nitroethane.

Similarly, normal propyl iodide and secondary propyl iodide react with hydroxylamine, forming *dipropyl-* and *di-isopropylhydroxylamines*, $(C_3H_7)_2NOH$.

Hantzsch and Hilland (*Ber.*, 1898, xxxi., 2058) have recently described their work on this subject. They generally confirm the account given by the authors five years ago of the reaction of methyl iodide with hydroxylamine. They assert that the hydrated base (see above) is really a carbonate. The authors have repeated their experiments, and find that there is no foundation for this statement. It is evident, from the different account given by Hantzsch and Hilland of the properties of trimethyloxamine, that the material they examined contained impurity, probably hydroxylamine.

By the reaction of ethyl iodide with hydroxylamine, Hantzsch and Hilland obtained only monethylhydroxylamine hydriodide. The authors have repeated their experiments, and have been unable to isolate any such substance. They find, as stated above, that diethylhydroxylamine is the chief product of the reaction.

Discussion.

Dr. HEWITT drew attention to Bamberger's recent discovery of the analogous dimethylaniline oxide by the direct oxidation of dimethylaniline by hydrogen peroxide (*Ber.*, 1899, xxxii., 342). The substance is destitute of reducing properties, and exhibits a peculiar transformation into a mixture of ortho- and para-nitrodimethylanilines by the action of nitrous acid. This transference of an oxygen atom from the dimethylamino- to the nitroso-group, thereby converting it into a nitro-group, may possibly be the analogue of the conversion of trimethyl oxamine into a mixture of dimethylamine and formaldehyde.

Dr. FORSTER remarked that distillation under atmospheric pressure resolves the benzyl ether of camphoroxime into benzaldehyde and camphorimine, a change suggesting analogy with the conversion of trimethyloxamine into formaldehyde and dimethylamine.

*37. "*Derivatives of αα'-Dibromocamphorsulphonic Acid.*" By ARTHUR LAPWORTH.

When ammonium α-bromocamphorsulphonate is heated with bromine and water at 110—120°, a dibromocamphorsulphonic acid is produced, identical with that obtained in small quantities by heating the salt with dilute nitric acid (*Trans.*, 1897, lxxi., 19; compare *Proc.*, 1898, xiv., 159), and its investigation has been continued with the following results:—

The *ammoninm*, *potassium*, *sodium*, *calcium*, *barium*, *zinc*, *cadmium*, and *lead* salts are readily soluble in water and crystallise well; the *basic lead* salt is amorphous, and is practically insoluble in water. *αα'-Dibromocamphorsulphonic chloride*, $C_{10}H_{13}Br_2O{\cdot}SO_2Cl$, is very sparingly soluble in the usual media; it crystallises in beautiful hemihedral forms belonging to the orthorhombic system, is isomorphous with the sulphonic bromide already described (*loc. cit.*), and melts at 203—204° with decomposition. The *amide*, $C_{10}H_{13}Br_2O{\cdot}SO_2NH_2$, forms hemihedral crystals, is very sparingly soluble in the ordinary media, and melts at about 238° with decomposition.

When αα'-dibromocamphorsulphonic chloride is treated with piperidine in ethereal solution, a mixture of *dibromocamphorsulphopiperidide*, $C_{10}H_{13}Br_2O{\cdot}SO_2NC_5H_{10}$, and *monobromocamphorsulphopiperidide*,—

$$C_{10}H_{14}BrO{\cdot}SO_2NC_5H_{10}$$

is obtained. The former crystallises in orthorhombic plates or prisms melting at 157—158°; the latter, which may also be obtained by the action of piperidine on α-monobromocamphorsulphonic chloride, crystallises in plates melting at 152°.

When dibromocamphorsulphonic acid is heated with strong alkalis, bromine is eliminated, and the product, on treatment with phosphorus pentachloride, yields α-monobromocamphorsulphonic chloride melting at 135°, the action being exactly analogous to that of alcoholic potash or soda on αα'-dibromocamphor.

When heated at its melting-point, αα'-dibromocamphorsulphonic bromide loses sulphur dioxide, yielding *αα'π-tribromocamphor*, $C_{10}H_{13}Br_3O$, This crystallises from dilute alcohol in fine needles and melts at 69—70°; it is rapidly decomposed when warmed with solutions of silver salts or with alkalis, the product with the latter being απ-dibromocamphor melting at 152°. The new tribromocamphor is also obtained by heating απ-dibromocamphor with bromine at 120° in sealed tubes; this fact and others which have been mentioned indicate that the dibromocamphorsulphonic acid has the constitution assigned to it by the author.

38. "*Ethylic ββ Dimethylpropanetetracarboxylate.*" By W. TREVOR LAWRENCE.

Meyenburg (private communication, compare *Ber.* 1895, xxviii., 785) attempted to prepare ethylic ββ-dimethyl propanetetracarboxylate by the condensation of ethylic isopropylenemalonate with ethylic sodiomalonate, but was unsuccessful, and, with his permission, the author has continued the work.

Ethylic ββ Dimethylpropanetetracarboxylate,—

$$CMe_2[CH(CO_2Et)_2]_2,$$

is formed in small amount in preparing ethylic isopropylenemalonate from acetone and ethylic malonate in the presence of acetic anhydride and zinc chloride. It is obtained readily by the interaction of molecular quantities of ethylic isopropylenemalonate with ethylic sodiomalonate in dry ethereal or benzene solution. The mixture is allowed to boil during twenty-four hours, a half molecular proportion of ethylic sodio malonate added, and the boiling continued during a further twenty-four hours. On fractional distillation in a vacuum, the compound is obtained as a thick oil boiling at 218° under 14 m.m. pressure. On hydrolysis with alcoholic potash it is converted into ββ-dimethylpropanetricarboxylic acid, $CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH(CO_2H)_2$, melting at 172°, and with sulphuric acid into ββ-dimethylglutaric acid,—

$$CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

melting at 101°, from which the anhydride melting at 123° was obtained.

The author is engaged with Dr. Herz in the further investigation of the properties of the substance.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, March 10th, 1899.

Prof. OLIVER LODGE, F.R.S., President, in the Chair.

Mr. A. A. CAMPBELL SWINTON described and exhibited the Wehnelt Current-interrupter.

A glass cell contains a large cylindrical negative electrode of lead and a small positive electrode consisting of a platinum wire about $\frac{1}{16}$ inch or $\frac{3}{4}$ inch in length in a solution of 1 part sulphuric acid to about 5 parts water. The platinum wire may project from the top of the shorter arm of a J-shaped ebonite tube, so that it can point upwards immersed in the solution. Or it may be fused into a similar glass tube; but glass is apt to crack in the subsequent heating. Wehnelt's interrupter replaces the make-and-break apparatus of an induction coil; it also replaces the ordinary condenser of that apparatus. In its present form it requires rather a strong current. The resulting spark at the secondary terminals differs in character from the ordinary spark of an induction coil; it is almost unidirectional, and in air takes a $\wedge$ form—bright, continuous, and inverted—somewhat like a pair of flaming swords rapidly crossing and re-crossing one another at their points. By blowing upon the $\wedge$ it breaks up, and then more nearly resembles the customary discharge of a coil. The sound emitted by the spark has a pitch that varies with the conditions of the circuit. As the self-induction of the circuit is diminished, the spark-pitch rises; it becomes infinite when the self-induction vanishes, *i.e.*, the Wehnelt interrupter will not work in a circuit devoid of self-induction. As the applied potential-difference diminishes, the spark-pitch diminishes. In Mr. Campbell Swinton's experiments, 25 volts was the minimum primary voltage at which his apparatus would work. The spark-pitch also varies with the length of the platinum wire electrode in the solution. If the circuit is closed by dipping this electrode into the solution, the apparatus will not work; the wire must be dipped in before closing the circuit. After working for about a quarter of an hour, the action often ceases; this fatigue-effect is not due to heating of the solution, for it is not obviated by keeping the temperature constant by a water-bath. It is supposed that the oxygen generated at the platinum electrode forms a more or less insulating film which interrupts the current until absorbed by the surrounding water. The fact that oxygen is more easily absorbed than hydrogen may explain why it is necessary to connect the platinum electrode to the positive pole of the battery or dynamo. When the platinum electrode is dipped gradually into the solution, the wire gets red-hot, and the interruptions do not take place. Again, when the apparatus stops from fatigue the platinum gets red-hot. The action is further complicated by a series of small explosions, and by the formation of a kind of electric arc at the platinum electrode. The coil exhibited was connected to the 100-volt electric light mains at Burlington House; in this case the potential difference at the terminals of the primary was 30 volts, and that across the interrupter 150 volts—a total of 180 volts, showing the effect of impedance. For Röntgen ray work the apparatus would be very effective, but unfortunately the sparks produce great heating, so that the cathodes of tubes are melted. Mr. Campbell Swinton suggested that, as the sparks were more nearly continuous than ordinary discharges, they might produce Hertz waves less rapidly attenuated than those now applied to wireless telegraphy; the trains of waves would also follow one another at shorter intervals than those from the sparks at present employed.

The PRESIDENT said he was rather surprised that the self-induction of the primary coil was not sufficient of itself to form the induction factor in the impedance necessary for perfect working. He would like to know how the apparatus behaved when an alternating current was used. Did the secondary coil become damaged by overheating? Did reversal of the current assist the recovery from the fatigued condition of the apparatus? The natural period of the circuit depended upon its capacity and its self-induction. There was undoubtedly capacity at the surface of the platinum electrode in the liquid; this capacity acted together with the auxiliary self-induction and the self-induction of the rest of the circuit in the orthodox way, and there was automatic adjustment of resonance to the frequency of the interruptions, probably by variations of the capacity at the electrode. The heating effect when a wire was made to close a circuit with a liquid was discovered many years ago.

Prof. G. M. MINCHIN thought that the usefulness of the apparatus would be greatly increased if it could be made to work with less current. He had himself succeeded with 12 applied volts, but not with 10 volts. As a tentative experiment he had used a horizontal lead plate —with disastrous effect, for the apparatus went suddenly to pieces. Explosions were frequently obtained, but they were not attended with much real danger. In a later and safer apparatus he used a platinum wire about $\frac{3}{4}$ inch long, projecting from a glass tube, around which the lead plate was bent. There appeared to be a definite depth of immersion of this wire, at which the apparatus worked with minimum current. In his apparatus, this critical position was when half the wire was below the surface of the liquid, the other half projecting into the air. He attributed the fatigue to the presence of gas about the electrodes, for he observed that a mechanical tap to the base of the apparatus restored the working condition.

Mr. ROLLO APPLEYARD pointed out that the improved result at half immersion observed by Prof. Minchin, taken together with the phenomena described by Mr. Campbell Swinton as to the effect of dipping the electrodes into the solution, suggested that the liquid immediately around the submerged part of the wire was at some instants in the spheroidal state. The breaking-down of the spheroidal state would be facilitated by heat lost by the immersed part to the non-immersed part of the wire. The capacity for heat of the non-immersed part, and the degree of roughness or smoothness of the immersed part, would thus appear as factors in the explanation. No doubt the evolved gases were the primary cause of the interruption of current, but the wire having once become red-hot the spheroidal condition would introduce a further cause of electrical separation between the wire and the liquid.

Prof. V. BOYS asked whether it was the liquid or the electrodes that became fatigued. Experiments should be made to determine the effect of variations in the hydrostatic pressure around the platinum electrode.

Mr. T. H. BLAKESLEY said that the rise of potential at the terminals of the interrupter proved that the arrangement possessed capacity. Such a rise of potential could not occur without there being capacity any more than it could without self-induction.

Mr. D. K. MORRIS described experiments he had made with a Wehnelt interrupter, using a 1 kilowatt transformer with a transformation of 4 to 5, intended for 10 ampères at 100 volts. The anode of the interrupter was designed to have an adjustable surface to correspond with the load on the secondary—a platinum wire at the end of a copper wire could be projected more or less through the drawn-out lower end of a glass tube containing oil. The best results with the interrupter were obtained with about 45 volts on the primary circuit. At this pressure, an average current of 1 ampère sufficed to give 125 (alternating) volts very steadily on the secondary. As measured by an electrostatic instrument, the "no-load" loss was only 45 watts. The secondary could then be loaded up with lamps, provided that the exposed surface of platinum wire was proportionately increased. The energy delivered to the lamps, however, was not at any load much greater thon 45 per cent of that taken from the mains. By connecting the interrupter with a condenser of $\frac{1}{4}$ microfarad, the efficiency at small loads was increased to nearly 60 per cent. He had observed that the fatigue of the interrupter could be temporarily remedied by reversing the current.

Mr. C. E. S. PHILLIPS asked whether Mr. Campbell Swinton had tried other liquids than dilute sulphuric acid. So far as his own experiments went, he had only obtained good results with that electrolyte.

Mr. CAMPBELL SWINTON, in reply, said that with the apparatus arranged in a simple circuit an alternating

current applied to the primary of an induction coil through a Wehnelt interrupter produced only about half the effect of the corresponding direct current—apparently only half the alternations got through. But if two interrupters were connected in parallel circuits, it was possible so to arrange them that one took one half and the other the second half of the alternations. It might therefore be possible to design an induction coil with two primary windings to correspond to the two interrupters, so as to give an additive effect. The induction coil he had used had suffered no damage from the currents employed in the experiments exhibited; there was extremely little heating of the secondary. He could not with his apparatus restore the working condition by any mechanical disturbance of the interrupter. Hydrochloric acid failed, but a saturated solution of potassic bichromate gave fair results.

The President, in proposing thanks, said he did not agree with Mr. Campbell Swinton's remarks as to the chances of improving Hertzian telegraphy by the use of these interrupters. The rate of interruption with this apparatus was something like 1000 per second, but the vibrations corresponding to Hertz waves were of the order 100,000 per second. The wave-trains from oscillations excited by the new interrupter would still be series of damped vibrations; the amplitudes would not be maintained. It might be advantageous to have sparks following one another so rapidly, but he doubted it. For Hertzian telegraphy, the spark at the oscillator should "crackle"; to produce the best effect, the air about the oscillator should be in a non electric condition.

A paper by Mr. A. Griffiths on "*An Apparatus for the Determination of the Rate of Diffusion of Solids dissolved in Liquids*" was then read.

The apparatus consists of a cylindrical glass vessel subdivided about midway by a horizontal non-porous partition into which are fitted a number of vertical tubes. The lower section of the vessel is filled with a liquid, such as an aqueous solution of cupric sulphate, and the upper one contains pure water. The method consists in determining by chemical analysis the quantity of cupric sulphate transmitted up the tubes. The paper gives the theory of the method, with very few experimental results. Ordinary diffusion observations are affected by the flow of liquid in the tubes due (1) to changes of temperature of the apparatus as a whole, (2) to differences of temperature throughout the liquid, (3) to local variations in volume produced by the process of diffusion, (4) to inequalities in the lengths of the tubes. Equations are given for determining the magnitudes of the sources of error, and certain numerical cases are worked out.

The same author also contributed a note on "*The Source of Energy in Diffusive Convection.*"

Diffusion tends to produce local changes of density, causing gravitational currents, which currents can be made to do work. By "diffusive convection" the author means these gravitational currents. The heat equivalent of the work done is determined in a particular case, *i.e.*, for a sub-divided vessel, as in the above paper, having two tubes of unequal length. He points out that the heat absorbed, owing to diffusion through one of the tubes, is independent of the mechanical motion of the liquid in that tube, and it is also independent of the length of the tube.

The President proposed a vote of thanks, and in doing so described an apparatus he had used for a thermostat. A double-walled cylinder of copper sheet, with a little water in the inter-space, is exhausted at atmospheric temperature until the water boils; it is then sealed up. Water-vapour is a powerful equaliser of temperature, and a vapour jacket of this kind is very efficient when it is required to maintain uniform temperature—not constant temperature.

Mr. Watson described the method of Mr. E. H. Griffiths, who used tap-water as a negative source and a gas flame as positive source—with extremely good results—as a thermostat for constant and for uniform temperature.

The meeting then adjourned until March 24th.

Address of the President,
Prof. Oliver Lodge, D.Sc., F.R.S.

February 10th, 1899.

In taking the Chair of this Society for one year, notwithstanding that I am a country member and therefore shall not be able always to be present, I am I daresay traversing the views of what is considered best for the Society by a minority of members. I have no knowledge that it is so, but it can hardly be otherwise. I hesitated myself for some time, but ultimately consented to be put in nomination by the Council; and I can promise that I shall try to be present as often as my duties permit.

I have been a member of the Society from its earliest infancy, for though not technically an "original member," nor one admitted in the first year, that is a mere accident of not having presented myself for admittance by the Chair; perhaps I had not paid my subscription, but I used to attend all the meetings, and my memory goes back to the preliminary discussions that preceded the birth of the Society, between Prof. Foster, Prof. Adams, Dr. Gladstone, Dr. Atkinson, and Dr. Guthrie, especially Dr. Guthrie, and to whom the idea of the Society was, I believe, largely due.

In those days we used to meet at South Kensington on Saturday afternoons; and my experience of recent years is altogether too remote and detached to make me aware whether the change, from the hospitable laboratory at South Kensington to the no doubt equally hospitable but less *physically* inspiring quarters of Burlington House, has been an unmixed advantage. If it is an unmixed advantage, the Society has been fortunate.

Our death-roll for the past year contains the names of two original members whose figures were familiar at the meetings in those early days: Henry Perigal and Latimer Clark. It also contains the names of Sir J. N. Douglass, so well-known in connection with lighthouse work; of Dr. Obach, the skilled electrician and designer of Messrs. Siemens Bros.; of the Rev. Bartholomew Price, known not only as a mathematician but also as a man of public spirit and enterprise in the University of Oxford, who had I believe more to do with the early financial success of the Clarendon Press than is generally known; of Dr. J. E. Myers, and alas! of Dr. John Hopkinson.

It is unfitting that this year's deliverance from the Chair of any Society of which John Hopkinson was a member should fail to contain some reference to his untimely loss; yet there is nothing for me to say but what you already feel, and no words of mine are needed. I cannot say that I knew him in his youth, but I heard of him. He and I as self-taught students—at least, I was at that time self-taught, and he could hardly have found a better teacher than himself—once figured together in the so-called honours list of the South Kensington May examinations in Electricity and Magnetism, or else in Sound, Light and Heat, or in both. Needless, to say, his name stood above mine. He passed, for fun, in nearly the whole range of South Kensington subjects; I took a good many of them, but had nothing like either his comprehensive range or his educational advantages. And then he went and wrested the Senior Wranglership from that exceptionally brilliant mathematical genius, J. W. L. Glaisher. That was a surprising achievement for a Whitworth Scholar and practical Engineer. May I be allowed to congratulate Mrs. Hopkinson and her family not only on a peculiarly noble donation, but also on its special application to the welding together the names of Cambridge, of Engineering, and of Hopkinson.

It is remarkable, as Mr. Arthur Balfour said in a speech the other day (at the opening of the Battersea Institute, I

think), it is remarkable how in modern times the pursuit of science tends in the direction of rapid and immediate application.

In Newton's time pure science was altogether aloof from practice: I do not suppose that the gravitational theory of astronomy had any effect on His Majesty's coins at the Mint, nor did the prismatic sifting of white-light lead at that time to any chemical applications of spectrum analysis. Even as late as Faraday's day the induction of currents by motion and magnetism exercised no appreciable effect on commerce and industry.

Nowadays, Fourier's theorem is applied by Lord Kelvin to work on Atlantic cable; Hopkinson's researches on the magnetic circuit (an idea that has revolutionised the practical treatment of magnetism) result at once in improvements in the dynamo; and Hertz's experimental detection of Maxwell's waves seems likely to result before long in a new system of wireless telegraphy.

What is the cause of this keen interest in practical applications felt in varying degrees by nearly all modern physicists, felt most keenly and consistently I think, of those I know, by your past-President Prof. Ayrton? Is it the example and inspiration of Lord Kelvin, or is it that the human race generally is beginning to be better educated than it used to be, to take more kindly to the result of scientific researches, to be more eager to learn about them, and, if possible, to apply them; partly, no doubt, because it has gradually discovered that by judicious treatment it can convert them into substantial commodity?

Surely, on the whole, with some drawbacks, the result from the point of view of science is good. If science were really remote from all human use or interest, as some scoffers still endeavour to maintain it to be, would there not be a fear lest gradually the human race should get tired of it, should cease to encourage even by approval or applause those whose instinct or mission it might be to develope it? So that gradually a blight might settle down, and advanced scientific knowledge become as extinct as a dead language or a fossil genus. A few scholars here and there would take an interest in it, as they did in the Middle Ages, and it might perhaps for a time be instilled into youth at the point of a cane, as the dead languages not so long ago used to be; but unless a branch of learning enters in some way into the life and well-being of a community, unless it has aome real interest—a literary interest it may be, a commercial interest perhaps, a living human interest of some kind—there is fear that, however artificially bolstered up it may be for a time, by those whose stock in trade it is and who know little else, it will ultimately be suffered to go by the board and become to all practical intents and purposes dead, buried, and extinct.

I said just now that I supposed the public as a whole were gradually getting better educated, but how miserably slow is the process and how lamentable the present result. I have no feud with orthodox secondary schoolmasters, indeed some of them are my very good friends, but is it not painful to be unable to speak to the average so-called educated Englishman (except a few here and there of course) on any scientific discovery without at once being met by a hopeless wall of ignorance?

Is it so in other countries? I hardly think so; I do not think it is so marked even among Scotchmen, at any rate not among Scotchmen who have had their Natural Philosophy year at the University. A year for training in the whole of science—it is not much. If scientific men were ignorant of letters in the same proportion they would hardly be able to read, except in words of one syllable, nor write, except with the laborious contortions of the village urchin; a year extended on the subjects of all the Arts would not carry one very far. And as to sums, how many men there are whose mathematical equipment is limited to the practice of compound addition and subtraction, and who shy if they see an algebraic symbol, even in a newspaper—indeed, when they occur in newspapers they are often of a kind that deserve to be shyed at.

They learn languages, some people seem to enjoy learning foreign languages—though the multiplicity of them is an artifical arrangement which an international convention might alter if it choose—but the exact and beautiful language in which a great part of science is and must be written is to the majority of men unknown. Are teachers wholly free from blame in respect of the dislike which many boys feel for the most elementary mathematics, for problems which may be made exhilarating when properly presented? I believe they are not. If the teacher dislikes mathematics, the boys will hate it, and if they hate it when young they will love it but little better when they grow up and proceed to be teachers themselves. There is a law of geometrical progression or compound interest here, and it seems to have been at work for some time. I must not, however, be understood here to be speaking of really cultivated intelligences or authorities in any subject. A thorough training in any branch of knowledge may so stimulate and enlarge the faculties as to fit them for intelligent appreciation and criticism of many other branches. Some men of letters I know whose minds are copiously and essentially scientific, they have not the detailed knowledge of the professed worker in science—that would be impossible and unnecessary—but they appreciate and assimilate all the main doctrines of science, and their broad criticisms and suggestions are often of value to the special worker. Any educational strictures on which I have ventured have reference not to scholars but to average people; at the same time I believe many scholars feel their deficiency in mathematics, and I believe it to be the result of bad teaching.

This is not my Address, it is a preliminary excursus, my Address has reference to a physical problem which has interested me, and about which I thought it might be interesting if I said something. It is customary to review some topic in an Address, not to adduce anything specially new, but to treat of or attempt to clarify something already known. Usually it is some experimental fact which is thus treated, sometimes it is a point of theory; it is the latter to which I wish to ask your attention.

As to experiments, if I quickly review some of those that strike me in the past year—there is further progress to be reported concerning the developments of Prof. Zeeman's great discovery, the most important being (1) the new manifestations of it, or of a closely allied phenomenon, discovered by Professor Righi, to which Prof. S. P. Thompson called the attention of Section A at Bristol last September; and (2) some extension of the resolution of complex lines, discriminating between the effect as exhibited by different lines, a discrimination which seems likely to lead to an extension of the powers of spectrum analysis by the application of a magnetic field to the source of light, as studied with apparatus of splendid dispersive power by Prof. Preston, and with his own ingenious method by Prof. Michelson. There is a notable continuation of the remarkably powerful and beautiful researches into atomic properties carried on at Cambridge by Prof. J. J. Thomson; about which a great deal more might be said. And then there is the prediction made in the columns of *Nature* by Prof. G. F. FitzGerald, but not yet verified, that circularly polarised light sent through an absorbing medium would constitute a magnet.

Many have been the attempts, from Faraday downwards, to excite magnetisation by means of light, to detect a real and not an imaginary "magnetisation of a ray of light," but all the experimenters hitherto have failed to realise the necessity of an absorbent medium. The effect is bound to be small, and of course it may not be there after all, but I understand it is being looked for, and it has at any rate been on rational grounds predicted.

Dr. Barton has continued experiments on the damping of waves on wires, and has not yet reconciled a discrepancy between theory and experiment; being able, as I understand him, to account for only 5½ per cent of the out-

standing discrepancy. I have not myself looked into the matter, but I understand that a note has been communicated by Mr. Heaviside. I hope it will be published in full.

The subject of Terrestrial Magnetism, in the hands of Prof. Schuster on the theoretical side and of Prof. Rücker on the practical side, has recently entered on an enlarged existence, and seems to be taking up a position almost of an independent science, so that when the multifurcation or explosion of Section A occurs, as sooner or later I fear it must, the fragment entitled Meteorology and Terrestrial Magnetism will perhaps not be one of the smallest.

The publication called *Science Abstracts* has continued to be welcomed by workers all over the country, and the abstracts sent by Mr. Fournier d'Albe to the *Electrician* are also useful and admirably done. I have no knowledge myself of the mode of control of the publication of our *Science Abstracts*, but I confess to a personal preference for the older form, the one with a less startling cover, and with a list of authors' names, instead of unnecessary advertisements of well-known firms, on its back page. Undoubtedly the inauguration of these *Abstracts* supplies a long-felt want, and even if one does not always find time to read them it is a comfort to feel that there they are, to be read in some less pressing season; and one need not envy the German worker his *Beiblätter* as one used to.

But there is one most important event that has occurred during the year, perhaps to us conjointly as physicists the most important of all, an event of which the science of Physics will feel the effects—I trust the wholly favourable effects—for centuries to come: I mean the decision of the Government to begin on a small scale the inauguration of a National Physical Laboratory. If its effects are ever in any respects unfavourable to true science, a heavy indictment will lie against its future governing body, and against its Superintendtent or Physicist Royal.

I wish to congratulate Sir Douglas Galton, as well as to some extent myself, on the result, the speedy result, of our urging of the subject, within the present decade, on the British Association; and as a Physical Society I think we owe a debt of gratitude to the Committee appointed by the Treasury to examine into the question, whose members gave themselves an immense amount of trouble, travelling to Berlin and elsewhere to make themselves acquainted with foreign ideals, and altogether going into the subject with extreme thoroughness, scientific judgment, and public spirit. The chairman of the Committee was Lord Rayleigh, but during his absence in India the acting Chairman was constantly Professor Rücker, Mr. Chalmers represented the Treasury with urbane frugality, and to Prof. Rücker and Mr. Chalmers, as well as to the other members of the committee, I am sure you will agree with me our thanks are justly due.

The record of their labours and of the voluminous evidence which they obtained, to which evidence indeed several of us here contributed, is embodied in a Blue Book of more than usual interest and instruction. I commend the perusal of it not only to professed physicists, but to all scientific teachers and their advanced students, that they may learn what accuracy is, and what it is practically wanted for.

It is not for me as your President to touch at any length upon outside or political topics, but briefly I venture to think that the year 1898 has been a year of no ordinary good fortune, at least to the Anglo-Saxon race. A year, and a Government, which has witnessed and assisted not only the beginning of a National Physical Laboratory, but such great outside events as the Imperial expansion and co-operation of America (for America, and not the United States, it will now have to be called), the liberation of Crete, and the restoration of the civilisation of Upper Egypt, is a year upon which we can look back with satisfaction, and is a Government which, irrespective of party, we may legitimately congratulate, and even—though that I admit is unusual—thank.

Would that we could add to its laurels the commencement on wise lines of a real and comprehensive, dignified and progressive, genuine University of London.

NOTICES OF BOOKS.

The Elements of Physical Chemistry. By J. Livingston R. Morgan. New York: John Wiley and Sons. London; Chapman and Hall, Ltd. 1899. Pp. viii.—292. 12mo., cloth.

In this volume the author has undertaken to present the elements of the entire subject of Physical Chemistry in a compact treatise, together with the important and but little known applications of it to the other branches of chemistry. The treatment is of course mathematical, yet the calculus is only used in the derivation of some of the laws, and the book can be used by students not proficient in higher mathematics. The author acknowledges indebtedness to the works of Ostwald, Le Blanc, and Nernst, and makes no claim to originality, but he has succeeded in making some of the topics simpler and clearer than usual.

Chapters are devoted to the three states of matter, solution, the *rôle* of ions, thermochemistry, chemical kinetics, phases, and electrochemistry; the last-named being discussed in four sections—migration of ions, conductivity of electrolytes, electromotive force, and electrolysis and polarisation.

Dr. Morgan defines Physical Chemistry as "that branch of the science of chemistry which has for its object the study of the laws and theories governing chemical phenomena"; he prefers the term "Physical" to "Theoretical" chemistry, because the subjects treated lie in the border land between physics and chemistry, and because purely physical methods are used.

The volume is especially adapted to the use of undergraduates in Columbia University, New York City, but it also appeals to a much larger audience; it contains no descriptive chemistry, which is assumed to be known to those undertaking the study of this work. Students who master its contents will find the study excellent mental discipline, and will gain a higher idea of modern chemical philosophy than can be acquired from any one text-book bearing on the subject known to the writer. The book seems well adapted to the needs of electricians who would learn the modern aspects of chemistry in its relations to electricity.

A perusal of the chapter on Solutions shows strikingly the greatness of the mind of Faraday; although his conception of ions has been modified by Grotthus and by Arrhenius, the English philosopher has the honour of taking the first step in the right path.

Dr. Morgan's book is well printed, and is furnished with an Index. H. C. B.

Chemistry in Daily Life. Popular Lectures, by Dr. Lassar Cohn, Professor in the University of Königsberg. Translated by M. M. Pattison Muir, M.A., Fellow of Gonville and Caius College, Cambridge. Second Edition, Revised and Augmented. London: H. Grevel and Co., 33, King Street, Covent Garden, W.C.

This book is said to embody the *substance* of a course of lectures delivered by the author to a Society in Königsberg. On looking through the Table of Contents one cannot but be struck with the immensity of the knowledge embraced; in fact, the book seems to be a kind of encyclopædia of physical and chemical technology. Considering its moderate size, the natural result is a collection of very condensed scraps of information upon many subjects, in our opinion too far advanced to be of much interest to the general reader, and too meagre to be of value to the student. As an instance of the condensation

of the matter, on page 23, following a description of candles, the reader is introduced to the chemical elements, and within three short pages is involved in the composition and formula for methane, ethane, and propane! After a flying glance at photography there follows a description of Röntgen rays, which is singularly incomplete and not at all accurate; the author seems to have got into a tangle of Geissler tubes, millionths of an atmosphere, and cathode rays; an incorrect drawing is given to show the paths of the cathode and Röntgen rays from a tube that is now obsolete, and "the celebrated glass-blower Geissler" and "Röntgen" are the only names mentioned in the matter. Within three pages of this we find ourselves in the depths of bimetalism! One cannot help thinking that such hasty scraps of information, although perhaps in keeping with the spirit of the age, are of but little lasting value, either to the student or to the general reader.

Report of the Principal Chemist upon the Work of the Inland Revenue Branch of the Government Laboratory. For the Year ending 31st March, 1898. London: Darling and Sons. 1898.

The number of analyses and examinations made during the year amount to 65,313; this is a slight increase over the previous year. The business of the Laboratory is divided into two parts, viz., work in connection with the Revenue Department, and work in connection with other Departments.

The work connected with the Revenue Department has largely to do with beer, spirits, and tobacco; 11,018 samples of wort in various stages of fermentation were examined, besides 4436 samples of finished beer. Of the 60 samples of tobacco examined for adulteration, 35 were found to be genuine and 25 adulterated. The adulterated samples were of foreign manufacture, being either smuggled cake Cavendish or cut tobacco, bearing no label; 11,817 samples were examined for moisture.

The consumption of tobacco per head of the population appears to be steadily though slowly increasing, it being for the year dealt with in this report at the rate of 1 lb. 12¼ ozs.

Legal proceedings have been taken 414 times in respect to samples analysed in this Department, and the total penalties inflicted have amounted to £6517; 119 cases were for selling so called "Temperance" drinks containing an excess of proof-spirit.

In other Departments the number of samples examined was 3480; these include a very miscellaneous lot of articles, such as butters, paints, cements, paper, water, &c.

CORRESPONDENCE.

ABSTRACTS OF CHEMICAL PAPERS.

To the Editor of the Chemical News.

Sir,—The German Chemical Society having recently done away with the abstracts formerly published in the *Berichte*, and having acquired control of the *Chemisches Centralblatt*, the result has been a decided cheapening of both journals, to the advantage of everyone concerned.

In my opinion, and in that of many of my American colleagues, there is need for a first-class publication which will be for all English reading chemists, irrespective of nationality, what the *Centralblatt* is for Germans. The Chemical Society of London, in its Abstracts, issues a good synopsis of current literature; but this is practically inaccessible to most American chemists, who cannot afford to pay the rather high subscription price of 30s., which includes the *Transactions*. For us to duplicate the work would be sheer waste of energy; the London Society might consent to issue its Abstracts under separate cover, and at a separate and reasonable subscription price for non-members. Still better, the work might be undertaken conjointly by the London Society and the American Chemical Society. The American Society might, for example, supply the abstracts of American literature, which is already quite extensive, as may be seen by referring to the monthly review of American research published in our *Journal*. Joint publication would enable the American Society to urge upon its fourteen hundred members the advantages of subscribing for the "English Centralblatt," and thus considerably increase the circulation and diminish the cost. About one-half the members of the German Society take the *Centralblatt*, and it is to be expected that several hundred subscribers for a similar English publication might be obtained outside of Great Britain, if the matter were properly pushed.

I am prompted to make these suggestions by the fact that this subject is being agitated in this country, several local sections of the American Chemical Society having already expressed a desire for co-operation with the London Society.—I am, &c.,

H. N. Stokes,
President of the Washington Section,
American Chemical Society.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 7, February 13, 1899.

Heat of Formation of Anhydrous Lime.—Henri Moissan.—This constant has already been determined by Thomsen, who states the value to be +131·5 cal. This is, however, probably inaccurate, owing to the impurity of the calcium used. The author re-determined this constant by using pure calcium, which he prepared. The small crystals were placed in a cylindrical tube of platinum covered with a number of small openings a quarter of a millimetre in diameter. When the cylinder is placed in the calorimeter, a very little water enters, and the liberated water prevents the too rapid ingress of the water. It was found that 1 grm. of calcium was completely attacked in three or four minutes. The calcium was weighed previously, and also estimated as lime in the water of the calorimeter: $Ca+2H_2O=H_2+CaO_2H_2$ (sat. sol.). The heat of formation being 94·10 (mean of two determinations). From this can be deduced the heat of formation of anhydrous lime directly from its elements.

$Ca+O=CaO$ anhydrous	x cal.
$CaO+Aq=CaO_2H_2$ sat. sol.	+18·1 ,,
$H_2O=H_2+O$	−69·0 ,,
$Ca+2H_2O=CaO_2H_2$ sat. sol. . ..	+94·1 ,,

$$\therefore x + 18{\cdot}1 - 69 = 94{\cdot}1.$$

$$x = 145 \text{ cal.}$$

This number is considerably greater than that found by Thomsen.

Phosphorescent Strontium Sulphide prepared from Carbonate of Strontium and Sulphur Vapour.—J. R. Mourelo.—The apparatus used for the preparation of this substance consists of a long porcelain tube placed in a combustion furnace. Inside are two porcelain boats some distance apart. In one of these is sulphur in little pieces, and in the other natural strontium carbonate (strontianite) coarsely powdered. One end of the tube communicates with a nitrogen apparatus. The whole apparatus must be filled with dry nitrogen before the heating begins. The tube is then gradually heated, be-

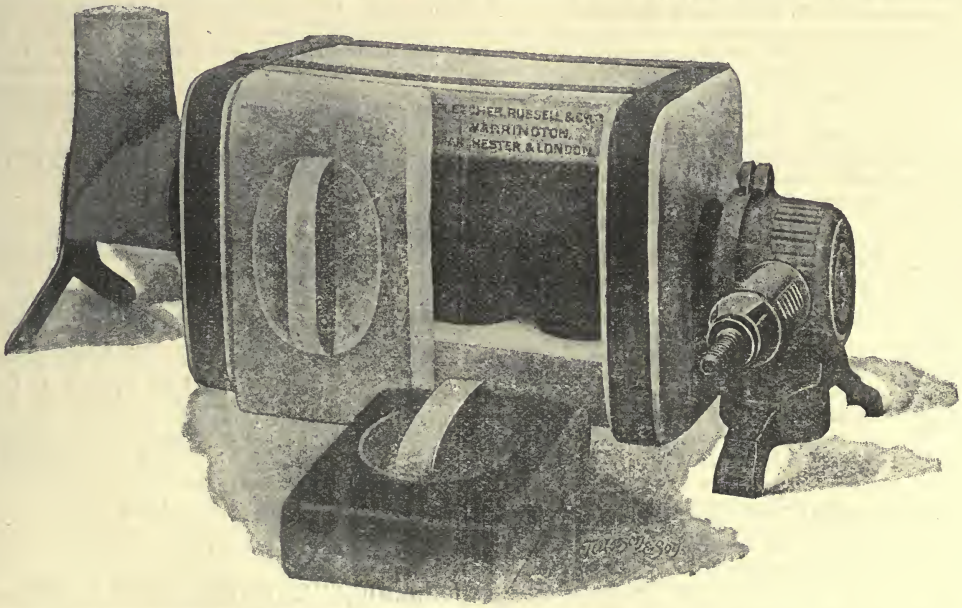
ginning from the end remote from the strontianite; the sulphur vapour, being slowly carried along the tube by the current of nitrogen, will gradually transform all the strontianite into sulphide. If pure strontium carbonate is used, the sulphide formed is not phosphorescent. The author finds traces of manganese in strontianite, which possibly affects the phosphorescence. He also draws attention to the fact that, if the sulphur vapour acts on the strontianite at a dull red heat, the sulphide is not phosphorescent. He makes a series of experiments on the influence of temperature on the formation of phosphorescent sulphide, and finds that there is a critical temperature above which sulphur vapour will always produce phosphorescent sulphide.

Combinations of Fatty Aldehydes with Mercuric Sulphate.—G. Denigès.—The results of treating ethyl and methyl aldehydes with mercuric sulphate are given. In the former case, the body $SO_4<^{Hg-O}_{Hg-O}>Hg.C_2H_4O$ is formed; in the second, mercurous sulphate is obtained.

Orthoxy-phenoxy-acetone.— C. Moureu.— Orthoxy-phenoxy-acetone, $C_6H_4<^{O-CH_2-CO-CH_3(1)}_{OH(2)}$, is produced when monochloracetone is heated on a water-bath with sodio-pyrocatechin. A description of its properties and of certain of its derivatives is given.

MISCELLANEOUS.

Laboratory Gas Furnace.—In the Chemical News for September 23rd last, on page 157, there appeared a description of a "New Laboratory Gas Furnace," illustrated with a woodcut. Messrs. Fletcher, Russell, and Co. send us the accompanying drawing, from which it is seen that the furnace previously illustrated is almost identical



with one which Messrs. Fletcher, Russell, and Co. inform us has been made by them for the last fifteen or twenty years.

The World's Wheat Supply.—The wheat problem of the future as recently presented to the world by Sir William Crookes has met a whirlwind of criticism. But the more the subject is examined the more clearly it appears that Sir William is not an idle alarmist. Among the latest analyses of the subject is a paper in the *North American Review*, by John Hyde, Statistician of the Department of Agriculture, under the caption "America and the Wheat Problem." Mr. Hyde carefully reviews the production statistics, computes the area of available wheat lands, and arrives at the conclusion that in 1931, when the population of the United States is estimated to reach 130,000,000, it will be a serious task for this country to supply its own wheat consumption, assuming that the soil may maintain nearly its present supply of nitrogen. It is not probable, however, that the soil will retain its fertility unless, as Sir William Crookes has suggested, the laboratory comes to the assistance of the farmer. In the principal wheat-growing regions the soil is being robbed of its accumulated nitrogen with hardly a pretence of restoring it. The leguminous plants, such as clover and cowpeas, do not thrive upon these lands, and, even if they did, the resort to rotation would reduce their yield by limiting the wheat crop to every alternate year. In the older sections of the country the rotation with legumes is extensively practised, but clover utterly refuses to grow on some lands, so they are being either robbed of nitrogen or fertilised by the extremely expensive commercial preparations which cannot profitably be employed in wheat growing. There is one source of supply of nitrogen that may be made available, at least temporarily, without waiting for the development of the Crookes idea of extracting it directly from the atmosphere. That is the utilisation of the ammonia by-product from coke-making. Of course this supply is not equal to keeping pace with the wheat production of the world for any great period of time. Utilisation of the supply wasted in the form of sewage, to the detriment of the public health, is also to be considered as practicable and of great consequence, and the time has come for serious consideration of this branch of the subject, both from the economic and the sanitary standpoint. These two sources of nitrogen supply should be able to tide the world well over the period named by Sir William Crookes—a single generation. But it is by no means certain they will suffice for two generations if wheat consumption continues at anything like the present *per capita* consumption. This "if" is an important factor in the problem, since it is quite as probable that civilised man will change the proportion of wheat in his food supply as that he will be obliged to resort to laboratory extraction of nitrogen from the atmosphere. A taste may be cultivated for cowpea flour.—*Pittsburg Dispatch.*

MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Royal Institution, 3. "The Morphology of the Mollusca," by Prof. E. Ray Lankester, M.A., LL.D.
—— Society of Arts, 4.30. "The Commercial Development of Germany," by C. Rozenraad, F.S.S.
WEDNESDAY, 22nd.—Society of Arts, 8. "Electric Traction," by Philip Dawson.
THURSDAY, 23rd.—Royal Institution, 3. "English Playhouses in the Sixteenth, Seventeenth, and Eighteenth Centuries," by Willian Poel.
FRIDAY, 24th.—Royal Institution, 9. "Transparency and Opacity," by The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
—— Physical, 5. "On the Criterion for the Oscillatory Discharge of a Condenser," by Dr. Barton and Prof. Morton. "The Minor Variations of the Clark Cell," by A. P. Trotter.
SATURDAY, 25th.—Royal Institution, 3. "The Mechanical Properties of Bodies," by The Right Hon. Lord Rayleigh, F.R.S., &c.

TECHNOLOGICAL EXAMINATIONS, 1899.
CITY AND GUILDS OF LONDON INSTITUTE.

The Institute's Examinations in Technology will be held on April 26th, 29th, May 1st, 2nd, 3rd, 4th, 6th, 8th, 9th, 12th, 13th, June 3rd and 10th.

All applications from Local Secretaries for examination in Technology must be forwarded to the Institute on or before March 20th.

Only in exceptional cases, and by payment of an additional fee, can applications be received from Local Secretaries after that date.

Candidates in Technology not attending any registered class should apply at once to the Secretary of the nearest Local Centre.

Applications from any individual candidates for examination at the Offices of the Institute should be made not later than March 30th, addressed to the Examinations Department, City and Guilds of London Institute, Exhibition Road, London, S.W., and should be accompanied by a Postal Order for the amount of the fee—the Subject and Grade of Examination being clearly stated.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2052.

THE BOILING-POINT OF LIQUID HYDROGEN AS DETERMINED BY A RHODIUM-PLATINUM RESISTANCE THERMOMETER.*

By JAMES DEWAR, LL.D., F.R.S.

The difficulties in liquefying hydrogen caused by the presence of air in the gas have been referred to (*Proc.*, 1898, xiv., 130), and later experiments have had for their object the removal of this fruitful source of trouble. This is by no means easy, as quantities amounting to only 1/1000 per cent accumulate in the solid state, and eventually choke the nozzle of the apparatus, necessitating the abandonment of the operation. Within the last week the author had succeeded in obtaining 250 c.c. of colourless liquid hydrogen, and this had been employed in a re-determination of the boiling-point. Earlier observations, made with a platinum resistance thermometer, had given −238° as the boiling-point, and a new thermometer, constructed from pure platinum from a different source, gave practically the same result. As this might be affected by some constant error, the determination was checked by employing a thermometer constructed from an alloy of rhodium and platinum, containing 10 per cent of the former. Alloys had been shown by Professor Fleming and the author to differ from pure metals in showing no sign of becoming perfect conductors at the absolute zero of temperature, and a study of the rhodium-platinum alloy had shown that the change in conductivity produced by cooling from 0° to the boiling-point of liquid air is regular, and may be represented by a straight line. As determined by the rhodium-platinum thermometer, the boiling-point of hydrogen was found to be −246°. Two ways of explaining the discrepancy between the two determinations suggested themselves. Pure platinum, although its resistance may be represented by a straight line almost down to the solidifying point of air, shows signs of a departure from regularity at about this point, and the curve may become asymptotic at lower temperatures. On the other hand, the resistance of the rhodium-platinum alloy diminishes less rapidly at these lower temperatures, and is much higher than that of pure platinum under similar conditions. It follows that its resistance-temperature curve, in all probability, deviates less from a straight line than is the case with platinum. Either cause would explain the differences observed, but the lower boiling-point, −246°, or 27° absolute, seemed to be the more probable, as it agreed very fairly with the value for the boiling-point calculated by the author from Wróblewski's results and that arrived at by Olszewski. As the use of other pure metals or alloys could not lead to more satisfactory results, the problem must be attacked in a different way by means of an "air" thermometer containing hydrogen under diminished pressure.

Addendum, March 17, 1889.—Since this paper was communicated the author has made a first attempt at determining the boiling-point by a constant volume hydrogen thermometer working under diminished pressure. The result is that this thermometer, which gave the boiling-point of oxygen as 90·5° absolute or −182·5°, gave for hydrogen 21° absolute or −252°. The three determinations that have been made are then as follows:—(1) pure platinum resistance thermometer 35° absolute; (2) rhodium-platinum resistance thermometer 27° absolute; (3) hydrogen thermometer 21° absolute. From this it appears that the boiling-point of hydrogen is really lower than was anticipated.

* A communication made to the Chemical Society, March 16th, 1899.

ON HYDROGEN PEROXIDE AS THE ACTIVE AGENT IN PRODUCING PICTURES ON A PHOTOGRAPHIC PLATE IN THE DARK.*

By W. J. RUSSELL, Ph.D., V.P.R.S.

(Concluded from p. 125)

In former papers it has been shown that the active bodies, both metallic and organic, are able to act on a photographic plate even when thin layers of many different substances are interposed; for instance, if a thin sheet of gelatin be laid on a polished zinc plate it only very slightly modifies either the sharpness of the picture or the time required for its production. If the gelatin plate be thicker the action will still pass through, but the picture will be more indistinct, and the time necessary for its production longer. If a 2 per cent solution of hydrogen peroxide be poured into one of the small glass dishes, and a sheet of gelatin 0·0013 inch thick be placed over it ¼ inch above the liquid, a picture will be obtained in fifteen minutes. If the sheet of gelatin be 0·008 inch thick, then the exposure must be for one hour; and if the gelatin be 0·01 inch thick, an exposure of three hours is necessary. If a sheet of celluloid be substituted for the gelatin, and it be 0·005 inch thick, the action still passes through, but more slowly than through the gelatin, and the plate now requires one hour exposure to give a good picture. With a plate of celluloid of double the above thickness, the exposure must be four times as long; and if the thickness be 0·033 inch, the time of exposure has to be 30 hours. These determinations show well what happens in these cases, but are only good approximations, not standard results. In addition to gelatin and celluloid, guttapercha tissue, india-rubber tracing paper, collodion, albumin, gold beaters' skin, parchment, &c., also allow the action to take place through them, and the obvious question which presents itself is: If hydrogen peroxide be the body which gives rise to the action, how does it pass through these different bodies? Take the definite case of zinc, if a plate of this metal be rubbed with coarse sand-paper and placed in contact with a photographic plate, a clear and sharp picture of the scratches is obtained, and it might have been expected that when the action took place through even a very thin sheet of gelatin the picture of the scratches would have no longer been visible, or at least only indistinctly so, but experiment shows this is not the case. How then does the peroxide permeate the gelatin? Not by the ordinary process of diffusion, for hydrogen cannot diffuse through it, so that it must be by a process of dissolving, or very feebly combining with the medium, or with a constituent of it, and thus travelling through escape on the other side. That the action is of this nature seems rendered probable by the following experiments, which show, at least to some extent, what takes place.—

A 2 per cent solution of hydrogen peroxide was placed in a dish with a sheet of the thinnest gelatin about one hundredth of an inch thick; above it and on the gelatin a photographic plate was placed, and allowed to remain there for twenty minutes. No picture was formed. Immediately on removing this first plate from the gelatin, a second one was put in its place, and allowed to remain there also for twenty minutes. This plate gave a faint picture, the third one gave a darker picture, and the fourth one was still darker; but the fifth, sixth, and seventh plates were, as far as could be judged by the eye, of the same degree of darkness. Thus the amount of peroxide given off on the upper surface of the gelatin went on increasing for one hour and twenty minutes, and then the action became uniform. The same kind of action occurs if zinc be used in place of peroxide solution. If a thin sheet of gelatin be laid on a piece of zinc and allowed to remain there for a week, then, on placing above it a sensi-

* A Paper read before the Royal Society, March 2, 1899.

tive plate, a picture will be produced in about one-third to one-fourth the time which would have been necessary if the previous exposure to the zinc had not taken place. Celluloid was found to act exactly in the same way as the gelatin. The plate, after the first half hour's exposure, gave no pictures, but a faint one after the second half hour; and it was not till after the fourth half hour that the action became constant. A thicker specimen, 0·011 inch thick, was also examined after intervals of two hours; it acted in the same way as the other specimens, but required ten and a half hours before the action became uniform. If drying oil or copal varnish be used in place of the peroxide of hydrogen solution, analogous results are obtained. This action explains how pictures can be obtained from invisible originals. If, for instance, a piece of white cardboard or paper is placed behind a copper stencil and is exposed to the vapour from peroxide of hydrogen solution, drying oil or copal varnish, &c., the exposed part of the paper becomes active, although not visibly affected, and on placing it on a sensitive plate, a picture of these parts is produced. Zinc acts in the same way, but only slowly. A zinc ornament, laid on a piece of Bristol board for eight months, charged the board only so far as to enable it to give a faint picture.

Gelatin can be substituted for the paper in these experiments, and can be charged and made to convey a clear picture to a sensitive plate. It is then evident that the action arising from zinc and other active bodies can, by an intermediate and inactive substance, be carried away and allowed to expend itself at another time and at another place.

With regard to the transmission of the action through gelatin, the water which it contains is probably the body which enables the peroxide to pass through. It can also be shown that it aids the transmission of the action through other inactive bodies; for instance, if Bristol board in its ordinary condition be placed on a polished piece of zinc, the action of the zinc only slowly passes through it, but if the board be damp the transmission takes place much more rapidly. The following comparative experiments illustrate this. Two similar pieces of Bristol board were taken, one was dried and then placed between a piece of perforated zinc and a sensitive plate and put under a bell jar with calcium chloride; the other piece of Bristol board was suspended over water until it was thoroughly damp and then placed between perforated zinc and a sensitive plate under a bell jar with a little water present. Both experiments were continued for twelve days, when it was found that with the dry board there was no picture produced, but with the damp one there was a good and dark one. If copal varnish be used in place of zinc, similar results are obtained, and if parchment be substituted for Bristol board the results are the same.

These experiments are, however, not conclusive, for it has been shown that with additional amount of water some of it finds its way to the zinc, and there induces the formation of more peroxide, which may account for the darker pictures. Even with the terpenes the additional amount of water may induce the additional formation of peroxide. This objection can, however, be obviated by cutting off the moisture in the damp medium from the active substance, or by using the aqueous solution of the peroxide as the origin of the action. In order to stop the aqueous vapour from either passing from the damp Bristol board or to it from the peroxide solution, a piece of tracing paper is interposed which allows the action to pass through it, but not any appreciable amount of aqueous vapour. On placing a sheet of tracing paper over a glass dish containing the peroxide solution and above it dry Bristol board with a photographic plate, in one and a half hours just an indication of a picture was produced, but when under the same conditions Bristol board which had been over water for nineteen hours was used, then a dark picture was formed. Again, similar experiments were made using a not highly glazed paper in place of the Bristol board, and the results were the same.

In place of tracing paper, celluloid was used and the dry Bristol board gave, under similar conditions, no picture, but the damp one a very distinct picture. In order to avoid having so much water present, plaster of Paris set by a little of the peroxide solution was used in place of the aqueous solution, and exactly similar results were obtained, so there is no doubt that hydrogen peroxide can readily pass through a porous body by the aid of water.

Alcohol acts in the same way as water, for when plaster of Paris wetted with peroxide solution was poured into a couple of similar dishes and allowed to set, and over one a piece of dry and over the other a piece of Bristol board moistened with alcohol were placed, and sensitive plates above them, after fifty minutes only a very faint picture was formed above the dry board, but a dark one over the wetted board.

Celluloid is, however, nearly as transparent to these actions as gelatin, and water in this case cannot be the transmitting medium, so that the question is whether there be any constituent of the celluloid which may act in a similar way to that of water in the gelatin. From the following experiments it seems that camphor can do so:—

Camphor itself, like water, is a perfectly non-active body. To obtain a thin non-porous layer of this body is difficult, but it is easy to prove that the emanations from hydrogen peroxide solutions, from zinc, copal, or other active bodies are readily absorbed by it, and readily pass through it. For instance, if a piece of camphor be placed about a quarter of an inch above a 2 per cent solution of hydrogen peroxide for seventeen hours and be then removed and placed on a sensitive plate for fifteen minutes, it gives a dark picture, and when a similar experiment is made, using drying oil in place of the peroxide solution, and the camphor be exposed to its action for three days and then brought in contact with the sensitive plate for one day, a dark picture is produced. This action can, however, be easily carried still further and proved to pass through even a thick layer of camphor. A piece 0·137 inch thick was placed about ½ inch above a 2 per cent solution of peroxide in a dish, for sixty-six hours, and a sensitive plate placed on the top of it; on treating this photographic plate with the developing solution it was found that a considerable amount of action had occurred. Thus the camphor which is a principal constituent of celluloid may enable hydrogen peroxide to pass through it.

That guttapercha and pure india-rubber should allow the action to pass through them is remarkable. The substance known as guttapercha tissue has a thickness of about 0·003 inch, and allows the action to pass readily through it; in fact, if even two thicknesses of this tissue be placed over the 2 per cent solution of the peroxide for seventeen hours, a dark picture is obtained. If the tissue be laid on a polished piece of perforated zinc and a sensitive plate above it, after remaining there for a fortnight a fairly good picture is obtained. If drying oil be used, the action will pass through the guttapercha in three days. With regard to this transmission of the action, although the chemical constitution of guttapercha is not well established, it is said to be a body related to camphor (Bernthsen, "Organic Chemistry," p. 509), and hence the action passes through it as it does through celluloid, and this is borne out by the fact that if a piece of guttapercha be placed for eighteen hours over the 2 per cent peroxide solution, and then placed for twenty minutes on a sensitive plate, it evidently has become active, for it then gives a good picture.

The above remarks apply also to india-rubber. The thinnest sheet that has been experimented with is 0·017 inch thick; this allowed the action to pass through it, but was too thick to give a picture, but, like the guttapercha, if placed over the peroxide solution it became active, and produced considerable action on a photographic plate.

With regard to other substances which allow the action to take place through them, the most interesting are true

gold-beaters' skin and albumen. If Bristol board or paper be carefully painted on one side with white of egg and allowed to dry in the air, it forms a medium through which the peroxide can pass. Collodion also allows the action readily to pass through it. In all these cases the tetra-paper may be used to confirm the results obtained.

Then with regard to bodies which do not allow the action to pass through them. Paraffin is one of them. If paper be painted with melted paraffin and it be placed over a solution of the peroxide, no action passes through, neither is it able to absorb the peroxide like camphor and india-rubber and guttapercha. A piece of paraffin placed over the peroxide solution for twenty hours and then tested by placing it on a sensitive plate produced no action.

Gum arabic is a body which sometimes is very opaque, but this is simply a question of hydration, and is confirmatory of what has been said before with regard to the action of water. Some unglazed paper was painted on one side with two coats of good gum arabic, and some of it was dried at 55° for some days, and another portion of it was *air*-dried only for some hours, and both were put over drying oil for three days. The dried paper gave only a very faint picture, but the more moist one a very dark picture.

When experimenting some time ago on the general nature of these reactions, polished zinc was placed below some inactive liquids to test whether any action took place through them. The small glass dishes were used, and a disc of bright zinc laid inside, and the liquid to be tested poured upon it; then the photographic plate was placed on the top of the dish. After remaining there for three or four days the plate was generally found acted on as if the zinc had been able to exert its influence upon it. Lately these experiments have been repeated and extended, and, as indicating the extreme delicacy of the reaction with the photographic plates, are of interest. The form of experiment was the same as described above, and the liquids used were alcohol, ether, ethyl acetate, chloroform, benzene, petroleum spirit. All these liquids were purified, so that when placed in the dish with the sensitive plate above them no action after a week's exposure took place. However, when a zinc disc was introduced below the inactive liquids the photographic plate was generally acted on, but with the benzene and petroleum spirit sometimes no action occurred. These rather singular results were next tested in another way. Portions of these inactive liquids were put into stoppered bottles with polished strips of zinc foil, and allowed to remain there for a week, and it was then found that the liquid had become active, for on testing it by putting it into a dish with a photographic plate above it, a dark picture was formed, so that the action of the zinc was to make the whole of the liquid active. Magnesium, cadmium, aluminium, fusible metal, and bismuth, all produced effects similar to those obtained with the zinc, but nickel, lead, tin, &c., produced no such effects. Further it was proved that a very small amount of peroxide rendered alcohol, for instance, very active; 0·1 c.c. of a 2 per cent solution of the peroxide added to 10 c.c. of alcohol gave it the power of acting on a sensitive plate ½ inch above its surface, so as to produce in a few hours a dark picture. The still more careful purification of these liquids, and especially the exclusion of moisture, was undertaken, and in every case it was found when all moisture was excluded that the zinc had no longer the power, when below a liquid, of acting on a photographic plate. Specimens of alcohol, ether, and chloroform were prepared, and these when placed in a dish with zinc at the bottom of it (standing over sulphuric acid) allowed no action to pass through them, and when treated for a week or more with bright zinc in a bottle, still retained their perfect inactivity. To a sample of the alcohol which in a dish with zinc allowed no action on the sensitive plate above to occur, a trace of water was added, as much as adhered to the end of a thin glass rod, and now with the same length of exposure a dark picture was formed. From these experiments, as well as those previously mentioned, it appears that this action on the photographic plate is one of extreme delicacy.

The action of water alone on zinc is interesting, and appears to confirm the view that hydrogen peroxide is the active agent in all these reactions. It has already been shown that although bright zinc is active, dull zinc is inactive. However, if a piece of bright zinc be placed in water and remains there for twenty-four hours or so, it, of course, oxidises, white spots or lines appear, and, in fact, in time the whole surface would become covered with oxide. Now the oxide thus formed is strongly active. Take the plate out of the water, let it dry, place it in contact with a photographic plate, and a strong picture of the spots of oxide is obtained. No doubt peroxide of hydrogen is formed, and remains entangled in this porous oxide; in fact it is difficult entirely to remove it. The plate, with this oxide on it, may be dried at ordinary temperatures and exposed to the air for a day or two, and the oxide is still active, or it may be dried over calcium chloride or even exposed to a vacuum for some time, and it is still active, but if heated to 55° for seventeen hours then its activity is gone and a picture the reverse of the former one is obtained; that is, the oxide is now quite inactive, but the metal itself is very slightly active. Oxides of zinc, cadmium, and magnesium, if wetted with peroxide of hydrogen solution, act in the same way and retain their activity with great pertinacity.

From the foregoing experiments it is then concluded that hydrogen peroxide is the agent which directly or indirectly causes the changes in the photographic plate.

This investigation has been carried on in the Davy-Faraday laboratory, and I would again tender my best thanks to the managers of the Royal Institution for allowing me to work there. My thanks are also due to Mr. O. F. Block, who has most efficiently helped in carrying on the above experiments.

THE ESTIMATION OF POTASH.

By E. WIGHTMAN BELL, F.C.S.

Of the various methods which have been advanced for the estimation of potash, the processes which are undoubtedly still considered the most reliable are those in which precipitation is finally made as the double chloride of platinum and potassium.

The majority of the more trustworthy processes involve the elimination of phosphoric and sulphuric acids, and the earthy and metallic bases, accomplished as a rule by a not inconsiderable number of precipitations, washings, and evaporations, tedious in themselves, and accompanied by a possibility of loss of potassium either by occlusion or as the result of imperfect washings.

The following process, which the author has used for some time, not only considerably reduces the time required for a determination, but also yields a precipitate of greater purity than is usually obtained. A chemical friend, to whom the process was communicated, has, after trial in the laboratory of a large manure-works, reported very favourably thereon.

In the case of *manures*, 5 or 10 grms. of the sample are well boiled with about 150 c.c. of water, with or without the addition of a little hydrochloric acid. Ammonia is now added in sufficient quantity to produce a slight alkalinity; then, *without filtering*, a considerable excess of barium carbonate (usually about double the weight of manure taken) is added, and the boiling continued for half an hour. The mixture is now filtered, the precipitate washed, and filtrate and washings made up to 500 c.c.

Fifty c.c. to 100 c.c. of the solution are then evaporated to dryness with the addition of a small quantity of ammonium oxalate, gently ignited, treated with hot water, and

filtered, the filtrate evaporated with hydrochloric acid and platinum chloride, and finished in the usual way.

Test analyses on mixtures of potash with superphosphate, bone, ammonium sulphate, sodium nitrate, &c., give results as under:—

Potash taken ..	0·1012	0·0500	0·2000	0·4250
,, found ..	0·1006	0·0498	0·2010	0·4230

In the case of *soils*, either the hydrochloric solution of the soil may be used (if K_2O soluble in HCl is required), and, after being rendered alkaline by means of ammonia, treated with barium carbonate, &c., as above, or the soil may be moistened with strong sulphuric acid, gently ignited, and the residue after boiling with water treated with barium carbonate, the boiling continued, filtered, and a portion of the filtrate then evaporated directly with hydrochloric acid and platinum chloride, without any previous addition of ammonium oxalate and ignition.

For the estimation of potash in *vegetable substances*, the organic matter should be moistened with sulphuric acid, ignited, and treated in a similar manner to soil.

A DELICATE REACTION OF HYDROGEN PEROXIDE.

By EDGAR S. BARRALET.

It is well known that solutions of hydrogen peroxide quickly oxidise the pale blue precipitate obtained by adding a solution of potassium ferrocyanide to a solution of a ferrous salt to "Prussian blue." Owing to the high colorific value of this pigment this reaction may be used as a delicate test for the presence of hydrogen peroxide,—in fact, for the detection of this compound in extremely minute quantities, since the oxidising agents, such as potassic bichromate, potassic permanganate, and calcium hypochlorite, cease to react at a far smaller degree of dilution.

Ten c.c. of hydrogen peroxide, 10 vols. = (3 to 3·2 per cent), were diluted to 100 c.c. with water; 10 c.c. of this diluted solution were now made again to 100 c.c. 20 c.c. of this solution diluted with water to 1 litre gives a solution of hydrogen peroxide containing 0·2 c.c. of hydrogen peroxide of 3 per cent strength, or approximately 1 part of H_2O_2 to 165,000 parts of water. Such a solution instantly intensifies the pale blue colour of ferrous ferrocyanide, 1 c.c. in 20 c.c. of the freshly precipitated compound being quite sufficient to make the reaction apparent. A similar addition of 1 c.c. of unboiled water has no effect. The ferrous ferrocyanide should either be freshly precipitated for each test or be kept in a bottle under a layer of petroleum.

ON THE COMPLEX SALTS OF PLATINUM OXALATES AND CHLORIDES.

By M. VÈZES.

I. Very little relation has yet been established by experiment between the two classes of saline compounds of platinum; on the one hand, the plato-oxalates, corresponding to the general formula $Pt(CO_2.CO_2)_2M_2$, in which M represents one atom of a monovalent metal, and, on the other hand, the chlorides, chloroplatinites $PtCl_4M_2$, and chloroplatinates $PtCl_6M_2$, which are the most frequently met with among the complex salts of platinum.

In particular the plato-oxalates appear to belong, by their constitution and properties, to the type of plato-salts, PtX_4M_2, to which the chloroplatinites belong; it also appears that they belong to this type through their method of preparation, and, further, that it should be possible to obtain them directly from the chloroplatinites by means of exchange reactions. Nevertheless the methods by which they are prepared up to the present do not depend on any of these simple relations; they all start from the more or less well-defined and difficultly obtained oxides. These methods, however, complicated from the theoretical point of view, are further difficult to carry out, and, as will be seen, not very applicable to the preparation of a notable quantity of the salts.

Doebereiner (*Pogg. Ann.*, xxviii., 180), who obtained the first oxalic derivative of platinum, prepared it by means of a badly defined and badly crystallised platinate of sodium, obtained by keeping a mixture of chloroplatinic acid and carbonate of sodium for a considerable time at a temperature of 100°; it appeared to correspond to the formula $Pt_3O_7Na_26H_2O$. This body dissolves, at the same time giving off carbonic acid gas, in a warm solution of oxalic acid, to which it imparts a very dark colour. The solution, when left to cool, becomes first green, then blue, and gives a deposit of fine reddish copper-coloured needles, which Dobereiner, without analysing them, took to be the platinous oxalate, C_2O_4Pt.

Souchay and Lenssen, in an extended research on the metallic oxalates (*Lieb. Ann. Chem.*, cv., 256), repeated Doebereiner's experiment, analysed the product formed, and assigned to it the formula $C_2O_4Pt+C_2O_4Na_2+4H_2O$, —that is to say, it is a double oxalate of platinum and sodium.

Söderbaum, who from 1885 to 1888 carried out a detailed research on the oxalic derivatives of platinum ("Studior öfver Plato-oxalylföremingar," 1888), finally prepared the same salt by also using Doebereiner's reaction, but he was much more careful in carrying it out. He prepared the platinate of sodium by the action of the chloroplatinate, $PtCl_6Na_2$, on an excess of melted soda, an operation which is difficult to perform, and dangerous to carry out on more than 15 grms. of material at one time.

The platinate obtained, mixed with carbonate of sodium, is then dissolved in a solution of oxalic acid heated on the water-bath: it is here important not to allow the temperature to rise above 70°, or else part of the platinum will be reduced to the metallic state. For the same reason it is far more convenient to work on small quantities of matter; Söderbaum only used 4 grms. of platinate for each operation. It can be seen from these details how complicated, inconvenient, and inapplicable this method of Doebereiner is, even when perfected by Söderbaum, for operations on a large scale.

The product thus obtained by Söderbaum is identical with the copper-red coloured needles analysed by Souchay and Lenssen; but this author, instead of taking it to be a double oxalate of platinum and sodium, considered it to be a complete salt, in fact a plato-oxalate, and represented by the formula $Pt(CO_2.CO_2)_2Na_2+4H_2O$. He justified this formula by preparing from this sodic salt the plato-oxalates of most of the other metals and a plato-oxalic acid $Pt(CO_2.CO_2)_2H_2+2H_2O$, from which all the preceding salts are derived.

These salts are all of a deep colour, analogous to that of the sodic salt just described; but most of them, when re-crystallised in a slightly alkaline solution, are changed into pale-looking crystals, totally different to the first crystals both in form and colour, having nevertheless almost exactly the same composition. Söderbaum, who was the first to observe this curious case of isomerism, and after him Werner (*Zeit. Organ. Chem.*, iii., 317), have both tried to explain this phenomenon by means of stereochemical considerations. It is more reasonable, however, to admit, as Werner has done in an hypothesis recently put forward (*Zeit. Anorg. Chem.*, 1896, xii., 50), that the plato-oxalates of the lightly coloured series are the only true plato-oxalates, and alone correspond to the formulæ given above; the salts of the dark coloured series being the products of the admixture of small quantities of unknown plato-salts with these plato-oxalates, corresponding to formulæ such as—

$$Pt(CO_2.CO_2)2Cl_2M_2,\ Pt(CO_2.CO_2)_2Br_2M_2,\ \text{or}$$
$$Pt(CO_2.CO_2)_2OM_2,$$

This hypothesis is rendered the more tenable by the already mentioned existence, among the salts of platinum, of other addition combinations of the same order,—for example, the so-called plati-cyanides of Hadow (*Chem. Soc.*, 1860, xiii., 106), which really correspond to the formula $5PtCy_4M_2+PtCy_4Cl_2M_2$; and also by the fact that the pale plato-oxalates pass easily to the state of their so-called copper-red isomers by careful oxidation with a little bromine or chlorine (Werner, *loc. cit*).

It is easily seen that none of the methods of preparation yet described are at all convenient; no one has made use of the relative compositions existing between the plato-oxalates and the other plato-salts, especially the chloroplatinites.

II. It is, however, possible to pass directly from the chloroplatinite of potassium to the corresponding plato-oxalate, from which all the other plato-oxalates can be produced; the change does not take place in an acid solution; even oxalic itself, in excess, is not able to displace the hydrochloric acid in these salts, but the reaction is, on the contrary, easily effected in a neutral solution.

To a warm concentrated solution of chloroplatinite of potassium we add an excess of neutral oxalate of potassium; we soon notice that the solution, of a deep red colour at first, takes a much lighter colour, and on cooling gives a deposit of straw-coloured prisms which act on polarised light. These characteristics suffice for distinguishing these crystals from the chloroplatinite which is of a deep red colour, from the chloroplatinate which is isotropic, and the oxalate of potassium which is colourless. Analysis shows, in fact, that these crystals are identical with the pale plato-oxalate prepared by Söderbaum.

	Calculated.		Found.				Söderbaum.
			I.	II.	III.	IV.	
Pt	194·8	40·16	—	—	40·45	—	40·35
2K	78·3	16·14	—	—	16·07	—	16·16
4C	48·0	9·89	—	—	—	10·36	—
8O	128·0	26·39	—	—	—	—	—
$2H_2O$	36·0	7·40	7·34	7·28	7·29	—	7·56
$Pt(CO_2.CO_2)_2K_2,2H_2O$	485·1	100·00					

Thus, this salt is prepared by the regular reaction of double decomposition:—

$$PtCl_4K_2+2CO_2K.CO_2K.CO_2K=Pt(CO_2.CO_2)_2K_2+4KCl.$$

This reaction, which recalls the preparation of the plato-nitrite of potassium by means of the chloroplatinite and an excess of nitrite of potassium, thus constitutes the most simple method for the preparation of the pale plato-oxalate of potassium. It justifies Werner's opinion, quoted above, according to which the pale plato-oxalate should be the normal plato-salt corresponding to the chloroplatinate.

The inverse reaction of converting the plato-oxalate of potassium into the chloroplatinite is just as easy to perform, but the solution must be acid, as Söderbaum has shown (*loc. cit.*, p. 74). It suffices to add to the solution of plato-oxalate an excess of hydrochloric acid, to cause its colour to pass from yellow to red; after concentration, it deposits, on cooling, chloroplatinite of potassium:—

$$Pt(CO_2.CO_2)2K_2+4HCl=PtCl_4K_2+2CO_2H.CO_2H.$$

The plato-oxalate of potassium can be also prepared in a direct manner from chloroplatinate of potassium, by a reaction analogous to that made use of in preparing it from the chloroplatinite.

If we heat to boiling, a solution as concentrated as possible, of chloroplatinate of potassium, and add to it an excess of neutral oxalate of potassium (more than 3 molecules for each molecule of the salt), carbonic acid gas is given off at the expense of part of the oxalate, which reduces the plati-salt to the plato-salt, and after prolonged boiling the solution, on cooling, deposits pale yellow crystals of plato-oxalate of potassium. These crystals, which are from chloroplatinate, if the boiling has been sufficiently prolonged, are easy to distinguish from this salt, both by their paler colour and more particularly by their action on polarised light. The transformation of the chloroplatinate into the plato-oxalate may be represented by the following equation:—

$$PtCl_6K_2+3CO_2K.CO_2K=$$
$$=Pt(CO_2.CO_2)_2K_2+2CO_2+6KCl.$$

It provides a new method for the direct preparation of considerable quantities of plato-oxalate of potassium from the most common compounds of platinum.

As can easily be seen from the facts quoted above, the theoretical relations which unite the plato-oxalates to the complex chlorides of platinum give simple and practicable methods for the preparation of these salts; inversely these relations are justified by the existence of these methods of preparation.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 22.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined by us during the month, all were found to be clear, bright, and well filtered.

We have again to record an excess of rain. The rainfall at Oxford during the past month was 1·92 inches, the average fall for the past thirty years is 1·76 inches, giving an excess of 0·16 inch, and making the excess for the first two months of the year 0·85 inch, or 21·6 per cent on the average fall.

It is interesting to observe the effect of the rainfall on the number of microbes in the unfiltered Thames water. No rain fell on the 1st, 2nd, or 3rd, and the average number of microbes in the Thames at Hampton up to the 4th was 6510 per c.c.; it then rained every day until the 15th, during which time the average number of microbes, including the 16th, rose to 38,354 per c.c.; after the 15th no more rain fell, and the average number of microbes from then to the end of the month fell to 14,914 per c.c.

This large increase in the number of microbes in the river, due to rain, originates not merely from the washing of the surface of the land, but is also largely due to atmospheric microbes brought down by the rain. As far as our experiments go they are perfectly harmless.

Our bacteriological examinations of 239 samples have

given the results recorded in the following table; we have also examined 37 other samples, from special wells, standpipes, &c., making a total of 276 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	2995
New River, filtered (mean of 24 samples) ..	19
Thames, unfiltered (mean of 24 samples) ..	23280
Thames water, from the clear water wells of five Thames-derived supplies (mean of 119 samples)	54
Ditto ditto .. .. highest	620
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	7481
River Lea, from the East London Company's clear water well (mean of 24 samples) . ..	68

During the month the London waters, chemically and bacteriologically, have maintained their high character as an efficiently filtered river supply.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

PROGRESS IN PHYSICAL CHEMISTRY.*

By THEODORE W. RICHARDS.

In these days of far-reaching specialisation the would-be speaker upon any subject is between a new Scylla and a new Charybdis. In order that his production should be comprehensible to those outside of the speciality it must almost inevitably be made boresome to those within the fold; but, on the other hand, that which is new to the specialist in his own topic is apt to be quite too new to the layman. Either popularising or specialising is likely to wreck the speaker's purpose by inducing at least a part of his audience to slumber, and this danger is especially imminent after dinner on a hot day which has been filled with mental effort. In this brief address, which Professor Smith has entrusted to my care, I shall probably run foul of both obstructions; but this irregular course will have the great concomitant advantage of permitting each class of hearers to obtain a few minutes of much needed repose.

We are rather accustomed to look upon physical chemistry as being a very modern invention, and in one sense we are not wrong in so doing. But after all, many of the fundamental generalisations of physical chemistry are by no means recent, and some of them are really old. Leaving out of account the probable discoveries in the subject made by Adam and Eve in the Garden of Eden, it is certain that the philosophers and alchemists were as much interested in those phenomena which lie on the border-line between physics and chemistry as in those which were purely physical or chemical. Indeed, the sharp line between the two subjects, drawn with so much emphasis twenty or thirty years ago, did not then exist. It is interesting to note that this sharp line is now rapidly being erased; we are realising more and more that the laws which govern one class of phenomena are applicable also to the other. Thus the cosmic working of the mind of man swings back and forth; will it ever come to rest upon the absolute truth?

In the middle of the seventeenth century, while this country was in an infantile condition, and Harvard College was little more than embryonic, Robert Boyle discovered his law relating to the contraction of gases under pressure—one of our most fundamental conceptions to-day. Lavoisier, before his tragic death in the Reign of Terror, forced upon a somewhat reluctant world the idea of the conservation of mass—an idea which perhaps had been assumed by some before—and in so doing laid a cornerstone of the great structure which was to follow. Only a few years later, Dalton, Avogadro, Ampère, Gay-Lussac, Dulong and Petit, Davy and Faraday, that prince of pioneers, with others less famous, made great additions to the world's thought in a physico-chemical direction. As far back as our forties Julius Robert Mayer and Helmholtz had acquired a clear grasp of the conservation of energy, while the other great law of energy had been partially realised by Sadi-Carnot two decades before. Hittorf's classical research on electrolytic conductivity, and Wilhelmy's epoch-making study of the speed of a reaction, a research upon the lines laid down by Wenzel and Berthollet so much earlier, took place over forty years ago. Only a decade later Guldberg and Waage laid down, in unequivocal and comprehensive terms, the fundamental law of mass-action, which is the basis of Wenzel's, Berthollet's, and Wilhelmy's observations, as well as of the progress and equilibrium of every other chemical change.

Why, then, with these foundations laid so far in the past, are we inclined to call physical chemistry a brand-new structure?

We all know that a part at least of the retarded development was due to the difficulty of dealing with solutions, which seemed anomalous in so many ways. Van't Hoff, by showing that a substance in solution followed many of the laws which would govern it in the aëriform state, and Arrhenius, by explaining in a simple way the differences between solutions conducting electricity and those which are non-conductors, cleared the track of these obstructions; hence for the last ten years the pace has been rapid. But it seems to me that there is another reason for the tardiness of the recognition of the importance of physical chemistry to be found in an unfortunate tendency observable sometimes in both chemists and physicists, a tendency which I am afraid we must call prejudice. Not only have untenable theories been held long after their time, but whole fields of study have been neglected by most chemists and physicists, because they lie on the border-line between the two sciences.

The average physicist only half realised that one of the most important relations of his great new force, electricity, is chemical, while the chemist does not always realise, even to this day, that Wheatstone's bridge and the telephone are chemical tools just as legitimate as, and no more "physical" than the thermometer, or the time-honoured balance, which extricated his predecessors from so hopeless a slough a hundred years ago. The day is fast approaching, however, when both chemist and physicist will welcome every mode of acquiring more light upon the absorbing topic which engages them in common—the study of the ultimate laws and structures of the universe.

It is a pleasure to think that one of the foremost of the brilliant men who have joined in advancing this wished-for end—this union of the resources of physics and chemistry to a common purpose—since the last meeting of the American Association has had its services recognised and his opportunity enlarged by his own University of Leipzig. Wilhelm Ostwald's new laboratory for physico-chemical research is the second important university building for this purpose which has been erected in Germany, the first having been built at Göttingen for the brilliant Walther Nernst; and the fact that Ostwald should at last have obtained a material outfit worthy of his unusual mental equipment is welcomed with enthusiasm by his many warm friends. We all know what a profound effect Ostwald's surprising book, his timely *Zeitschrift*, and in general his broad and progressive point of view, have had upon the development of both chemistry and physics, and it has been a matter of some surprise to many that so great an influence should have emanated from a laboratory so insignificant as the old Zweitem Laboratorium, so called. The new building,

* Address before Section C (Chemistry) of the American Association for the Advancement of Science, August, 1898.

although no very large, is in many respects a model; the architect and director of any kind of scientific workshop could not fail to obtain valuable hints from the detailed statement of it contained in the recently published appendix to the *Zeitschrift für Physikalische Chemie*. What a pity that America should allow Germany to outstrip us so far in devotion to the ideals of pure science! How long will it be before we build laboratories especially for physical chemistry, or even in many colleges allot a considerable share of old buildings to this end? And yet this physical chemistry now comprehends all of the field of theoretical chemistry, except a certain kind of reasoning concerned with the structure of organic substances, and the purely chemical part of the mysterious classification called the periodic system of the elements.

Very few of the processes of nature are simple in their proximate causes or their outward manifestations, however simple the grand underlying principles may be in their ultimate essence. The old maxim, by which theories were so often consciously or unconsciously judged, "Our theory is so simple that it must be true," is a dangerous guide. Geber's old notion that the whole world consists of sulphur and mercury, and the topsy-turvy delusion of phlogiston, relied largely on this maxim for support, and it behoves us to avoid similar mistakes. When the ancient idea of luck had been eliminated from scientific reasonings mankind admitted that every phenomenon is a function of its controlling causes; but that all the mathematical relations should be capable of solution, although to be sure only with the aid of the potent modern methods, is a new conception. In the old days problems in chemistry which could not be solved by simple arithmetic, or at best by elementary algebra, were considered incapable of quantitative solution; now, the higher mathematics is a facile tool in the hands of many an eager chemist. Even that mystery of mysteries, the smallness of the yield in the preparation of organic substances, has a flood of light shed upon it by the phase-rule and the mass-law!

No one who is familiar with the facts can doubt that the mathematical point of view will prove in the future more and more useful to chemists, as well as to the new physical botanists and zoologists, who are bringing it to bear on their transcendently recondite problems. These last-named investigators will follow in the footsteps of chemists, as chemists have followed in the footsteps of physicists.

The advance of the mathematical point of view in chemistry has brought with it an entirely new danger, as well as a new field of power. The accuracy of a result, of course, depends upon the accuracy of the foundation upon which the reasoning rests; and accurate mathematical processes may lead to wholly erroneous conclusions if they are based upon incomplete data. In chemistry this cause of error is especially prominent, because of the great complexity of most of the phenomena and the fact that they are often modified by subordinate influences. For this reason a physicist, used to simple phenomena and less complex effects, is especially apt, when he deals with problems allied to chemistry, to erect a large superstructure of mathematical reasoning possessing the semblance of reality upon a paper foundation, and be drearily awakened some fine day by the collapse of his air castle. The only mode of guarding against this subtle cause of disaster is to bring as much skill into every step of the experimentation as into the pure reasoning based upon the supposed facts. Here the physicist is seriously hampered by his lack of knowledge of chemistry, as well as by his usual repugnance to dealing with glass vessels and liquids; while on the other hand, the chemist is equally hampered by his inbred dislike of brass instruments and his imperfect acquaintance with the manipulation of his new sensitive tools.

In short, one must be an accomplished chemist, physicist, and mathematician in order to attain the highest results in modern theoretical chemistry, and the number of men who have the time or ability to acquire this threefold education can never be large. All honour to van 't Hoff, Ostwald, Nernst, and the others who come nearest the high ideal! While it is true, however, that few men can hope to attain the highest, it does not follow that the rest of us cannot be of great use. Each man can be of value in his own particular sphere; it is only necessary that he should work faithfully with a single eye to the truth, that he should be as free as possible from prejudice, and that his published work should be as accurate as he can make it. A well-conducted organic synthesis, a few carefully determined solubilities, will in the end be more valuable to the progress of science than a false generalisation, no matter how ingenious the latter may be. But how great is the responsibility of the collector of facts! for if his observations are false his work is of less value even than of the false theorist; it has not even ingenuity in its favour, and is worse than useless. Ostwald has more than once pointed to the responsibility attending publication, and we should all do well to heed his warning.

A comprehensive design which I had once harboured of giving you a *résumé* of the year's work in physico-chemical research throughout the world has been relinquished because of the great number of small papers which could not be treated satisfactorily in the brief space of an evening's talk. The subject of stoichiometry, in Ostwald's rather comprehensive interpretation of this word, has received this year the attention usually accorded to it. Solutions have still occupied many able men, without having by any means had their possibilities exhausted. Van 't Hoff's admirable little book upon double salts has already begun to exercise an effect upon the chemical world which the scattered and less illuminating papers of his students could not have been expected to exercise. Dr. Gibbs's interesting Address upon this important topic will undoubtedly excite further study on the whole question of the so-called "molecular compounds," which are so little understood and so hard to reconcile with our only partially satisfactory ideas of quantivalence. The far-reaching subject of chemical equilibrium is receiving more and more attention every year. There has been great activity in the fascinating field of electro-chemistry, and it is pleasing to see that some of the fundamental notions of this new science are coming to be recognised by the analyst and the technical chemist. Not least among the startling events of the year had been the supposed discovery of a number of new elements, crypton, neon, metargon, coronium, and etherion; if these really exist, we have here a series of brilliant chemical discoveries made solely by means of physical instruments and operations.

The most important of these interesting investigations are undoubtedly as well known to you as to your speaker, for in this day the sources of information are equally open to all; hence it would be a work of supererogation for me to discourse upon them in detail, even if there were time to do so. I prefer, therefore, to call your attention to some unpublished work with which you can hardly be so familiar; I mean the physico-chemical problems which have enlivened the last winter's laboratory work at Harvard. Since these covered a somewhat extensive field, their exposition may serve the double purpose of illustration and information. It is a pleasure to state that most of these researches would not have been thought of without the inspiring example and precept of the great men of whom I have spoken. The host of interesting investigations thus prompted in all civilised lands afford the best possible proof of the value of the modern physico-chemical hypotheses.

Dr. Gordon, the Harvard assistant in physical chemistry, has finished a very interesting series of measurements of the potentials of galvanic cells composed of metallic plates immersed in fused salts at high temperatures. After overcoming experimental difficulties too numerous to mention, he succeeded in obtaining constant values

which agree remarkably with Nernst's formula, and throw interesting light on the degree of dissociation existing in fused salts.

Mr. Edward Collins has nearly finished an elaborate attempt to verify Faraday's law with rigid exactness—an attempt which has met with greater success than any previous one.

Mr. G. N. Lewis made a series of careful measurements of the change of the potential of numerous reversible electrodes with the temperature, as well as a comprehensive revision of Meyer's inaccurate work on concentration cells involving amalgams of different strengths. In the thermodynamic discussion of the results Mr. Lewis arrived at some very interesting conclusions concerning strong as well as weak solutions of metal in mercury, and extended his experiment and mathematical analysis to the consideration of the potential of the unamalgamated metal in a solution of one of its salts. It is needless to say that this question is one of wide significance, but lack of time prevents my doing more than call attention to it now. Mr. Lewis's preliminary paper will appear early in the fall.

Mr. F. R. Fraprie spent much time in studying the eccentricities of inversion temperatures and transition intervals exhibited by the double sulphates of potassium and manganese. This problem proved to be far more complex and interesting than the similar case involving magnesium instead of manganese—a case which has been so carefully investigated under van 't Hoff's supervision. While Mr. Fraprie was not able to push the matter to completion, he obtained data enough to enable one to plot many of the most essential curves and to draw a mental sketch of the situation. It is hoped that this work may be continued during the present year.

Mr. Faber, in the course of a research having a more practical end as its chief aim, made a series of determinations of the solubilities of argentic halides in solutions of sodic thiosulphate, and obtained data which may be of use in determining the mechanism of this reaction. Messrs. Harrington and Henderson made a few interesting observations on some cases in which the dissolving of a solid in a solution caused a lowering instead of a rise in the boiling-point, and Mr. Churchill made a careful determination of the melting-point of crystallised Glauber's salt. The aim of this last labour was to secure a new fixed point for the standardising of thermometers, and we succeeded in showing that the point was as easily obtained and as constant at 32·484° as could be desired. This means of verifying thermometers will be a great boon to those who have not a standard instrument at hand. The paper will appear in the *Zeitschrift für Physikalische Chemie* and in the *American Journal of Science*.

Besides these varied researches, a protracted study of the causes of the occlusion and the unequal release of gases by the oxides of metals formed from the nitrates, occupied most of my spare time. It became evident that the excess of oxygen usually present in such material has a tendency to work its way out by a process of dissociation and re-combination which reminds one of the old-fashioned explanation of electrolysis. The nitrogen, not being able to escape in this fashion, is retained. This paper has just appeared in the *Proceedings of the American Academy*.

In addition to these, several other researches were also in progress, which, although they belong strictly to the domain of inorganic chemistry, would never have been undertaken but for the theoretical interests involved. Prominent among these were the revisions of the atomic weights of cobalt, nickel, uranium, strontium, and calcium, undertaken by Dr. Cushman, Messrs. Baxter and Merigold, and myself.

Of course, it sometimes happens that physico-chemical problems involving the use of complicated apparatus may be more readily solved in a physical than in a chemical laboratory, and in any case the co-operation of these two departments is highly advisable. I am happy to say that Dr. Duane and others have been conducting such chemico-physical investigations at the Jefferson Physical Laboratory of Harvard College, but of these I have no authority to speak.

When one has been discussing the past and present progress of any subject, it is natural that the mind should turn to the future also. What fields are likely to prove the most fruitful in the years to come? What researches will probably best advance the interests of science, and, therefore, of the life of man? Prophecy is always an uncertain business; but if one recognises the uncertainty it has few dangers, and becomes at least amusing. In this case, however, it presents few difficulties.

The whole field of physical chemistry is so fruitful when treated by modern methods that one can hardly single out any section as especially unpromising. Almost every subject is worthy of research; a more important question is the *spirit* in which the research is to be undertaken.

There have always been two parties as regards any question brought forward by mankind for discussion—the conservative party and the radical party. The former has a tendency to cling to old ideas simply because they are old, and the latter has a tendency to adopt new ideas simply because they are new. It seems to me that neither of these tendencies is legitimate. One should seek new points of view continually, but he should hold to that which is good until something is proposed which seems to him better. In every case he should weigh the respective arguments for and against the new point of view with a mind as free as possible from prejudice, and with a single eye to the truth. In short, the ideal investigator is the scientific independent, the chemical "mugwump." Is it too unreasonable to hope that the problems of the twentieth century will be dealt with in this thoughtful but untrammelled fashion?

We Americans rejoice in having on our side of the ocean the world-renowned names of several great men, of Wolcott and Willard Gibbs, of James Crafts, Edward Morley, the late Josiah Parsons Cooke, and others, who have combined chemistry with physics and mathematics; but, nevertheless, one must admit that America has not done as much as one could wish toward building up the fabric of modern physical chemistry. Although science is world-wide, and scientific men should be cosmopolitan, the existence of this Association proves that there is a patriotic side to the matter too. While welcoming the truth, wherever it is discovered, let us then do all we can to further its emanation from American laboratories and writing-desks.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 2nd, 1899.

Professor Dewar, F.R.S., President, in the Chair.

(Concluded from p. 125.)

39. *The Action of Metallic Thiocyanates on certain Substituted Carbamic and Oxamic Chlorides; and a New Method for the Production of Thiobiurets.* By Augustus Edward Dixon, M.D.

Acid chlorides containing the group COCl interact with metallic thiocyanates, in presence of suitable solvents, yielding the corresponding organic isothiocyanates; chlorine united with certain groups, other than carbonyl, is similarly exchangeable, but complete dechlorination is generally hard to effect. Experiments made with a view of ascertaining whether the halogen in substances generally acidic in character, or only that in direct union with a negative group, could thus be substituted, pointed to the latter as the determinant condition.

By heating with mercuric thiocyanate in presence of cumene, the chlorides of disubstituted carbamic acids are converted into isothiocyanates of the form $NR_2{\cdot}CO{\cdot}NCS$; these substances are related to the thiobiurets and to thioallophanic acid in the same way as ordinary thiocarbimides to thiocarbamides and thiocarbamic acid respectively. They unite spontaneously with nitrogenous bases, affording substituted thiobiurets, and, with benzylic alcohol, forming the corresponding substituted thioallophanates, $NR_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OBz$.

These thiobiurets may be regarded as thiocarbamides containing the carbamyl or $NR_2{\cdot}CO$-group; if so, the rule formulated by the author with respect to desulphurisation of the thiocarbamides by alkaline lead tartrate (*Trans.*, 1893, lxiii., 318) holds good, the carbamyl group here playing the same part as an alkylic or allyric radicle. Thus the thiobiurets, $NR_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHX$, can be desulphurised when X is an aromatic radicle, but not when it is aliphatic. Their behaviour as carbamylthiocarbamides (or thioureas) is further instanced by the production of thiohydantoin-like derivatives on treatment with chloracetic acid; the latter compounds are related to the biurets in the same way as the thiohydantoins to the thiocarbamides, and, in like manner, yield thioglycollic acid on hydrolysis.

The isothiocyanates could not be freed from the accompanying cumene by distillation either with steam or under diminished pressure; their solutions were used in preparing the following derivatives:—

1. *Diphenylcarbamylisothiocyanate*, $NPh_2{\cdot}CO{\cdot}NCS$, with aniline gives acc-*triphenylthiobiuret*,—

$$NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPH,$$

crystallising in white needles which melt at 163—163·5°, and yield phenylthiocarbimide when heated with acetic anhydride. a-*Orthotolyl*-c-*diphenylthiobiuret*,—

$$NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHTo,$$

from orthotoluidine, occurs in fine white needles melting at 163·5—164°. When desulphurised by silver nitrate it affords the corresponding *biuret*, $NPh_2{\cdot}CO{\cdot}NH\ CO{\cdot}NH\ To$, melting at 132—133°. a-*Paratolyl* c-*diphenylthiobiuret* melts at 172—172·5°, and resembles generally the ortho-derivative. a-*Methyl*-c-*diphenylthiobiuret* melts at 170—171°; the *ethylic* homologue at 137—138°, and the corresponding *benzylic* derivative at 167—168°. c-*Diphenylthiobiuret*, $NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2$, is precipitated on mixing the calculated quantity of alcoholic ammonia with the isothiocyanate solution; it forms long yellow prisms melting at 183°, and when fused with chloracetic acid yields n-*diphenylcarbamylthiourantoin*,—

$$NPh_2{\cdot}CO{\cdot}N{:}C{<}\begin{matrix}S{-}CH_2\\NH{\cdot}CO\end{matrix}{>}$$ (*Trans.*, 1897, lxxi., 638),

which is deposited from alcohol in tufts of flexible needles, melts at 184—185°, and is hydrolysed by potash, forming thioglycollic acid. a-*Benzylphenyl*-c-*diphenylthiobiuret*, $NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NPhBz$, from benzylaniline, occurs in white needles, becoming electrical on friction, and melting at 137—138°. a *Diphenylcarbamyl*-β *phenylthiosemicarbazide*, $NPh_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NHPh$, melts at 152·5—153°. *Benzylic*-a-*diphenyl*-β-*thioallophanate*, from the isothiocyanate and benzylic alcohol, occurs in vitreous, apparently rhombic, prisms melting at 141—142°; attempts to form similar compounds with methylic, ethylic, and cinnamic alcohols failed.

2. *Methylphenylcarbamylisothiocyanate*,—

$$NMePh{\cdot}CO{\cdot}NCS,$$

with aniline, yields a-*Phenyl*-c-*methylphenylthiobiuret*, $NMePh{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$, in woolly masses of needles melting at 158—159°. a-*Orthotolyl*-c-*methylphenylthiobiuret* forms thick, vitreous prisms melting at 108°; the *paratolyl* derivative occurs in white glistening plates melting at 156—157°. ac-*Dimethylphenylthiobiuret* forms leafy crystals melting at 90—91°. c-*Methylphenylthiobiuret*, $NMePh{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2$, crystallises in brilliant apparently clinorhombic, prisms melting at 166—167°; with chloracetic acid it yields n-*methylphenylcarbamylthiourantoin*,—

$$NMePh{\cdot}CO{\cdot}N{:}C{<}\begin{matrix}S{-}CH_2\\NH{\cdot}CO\end{matrix}{>},$$

a yellowish crystalline powder melting at 199—200°, and giving thioglycollic acid on hydrolysis. a-*Methylphenylcarbamyl*-β-*phenylthiosemicarbazide* crystallises from alcohol in brilliant prisms, melting at 119—120°; no evidence was obtained of the production of a stereo-, or other, isomeride. *Benzylic* a-*Methylphenyl*-β-*thioallophanate*, $NMePh{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}OBz$, forms vitreous rhombohedra melting at 90—91°.

3. *Ethylphenylcarbamylisothiocyanate*, $NEtPh{\cdot}CO{\cdot}NCS$, forms the following derivatives:—a-*Phenyl*-γ-*ethylphenylthiobiuret*, melting at 106—107°; the *orthotolyl* and *paratolyl* compounds, melting at 124—125° and 174° respectively. c-*Ethylphenylthiobiuret* occurs in large, greasy-looking flattened prisms melting at 147—148°, and yielding, with chloracetic acid, n-*Ethylphenylcarbamylthiourantoin*, melting at 184—185°. *Benzylic*-a-*ethylphenyl*-β-*thioallophanate* crystallises in colourless prisms melting at about 120°.

4. *Benzylphenylcarbamylisothiocyanate*,—

$$NPhBz{\cdot}CO{\cdot}NCS,$$

resembles its congeners in forming a yellowish solution which has no distinctive odour, and can be desulphurised in the cold by ammoniacal nitrate of silver, or by boiling with alkaline lead tartrate. a *Phenyl*-c-*benzylphenylthiobiuret*, $NPnBz{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$, occurs in colourless prisms melting at about 103°; the corresponding a-*Orthotolyl* compound melts at 131—132°, and when desulphurised, in presence of ammonia, by silver nitrate, yields a *guanidine*, $NPnBz{\cdot}CO{\cdot}NH{\cdot}C(NH){\cdot}NHTo$, melting at 136—136·5°. a-*Methyl*-c-*benzylphenylthiobiuret* forms white prisms melting at 99—100°; the a-*ethyl* derivative melts at 67—68°. c-*Benzylphenylthiobiuret* crystallises from a mixture of chloroform and alcohol in lustrous rectangular prisms; it melts at 179—180°, and with chloracetic acid yields the compound,—

$$NPhBz{\cdot}CO{\cdot}N{:}C{<}\begin{matrix}S{-}CH_2\\NH{\cdot}CO\end{matrix}{>},$$

a sandy crystalline powder, melting between 194° and 195°, and affording thioglycollic acid on hydrolysis by potash. *Benzylic* a-*benzylphenyl*-β-*thioallophanate* separates from hot alcohol in brilliant vitreous prisms melting at 133—134°.

5. *Oxanilylisothiocyanate*, $NHPh{\cdot}CO{\cdot}CO{\cdot}NCS$, is obtained from phenyloxamic (oxanilic) chloride and lead thiocyanate in presence of toluene; its solution, when mixed with aniline, yields a-*phenyloxamyl*-β-*phenylthiocarbamide*, $NHPh{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$: it melts at 172—173°, and slowly dissolves in hot potash, producing phenylthiourea.

40. "*A Reaction of some Phenolic Colouring Matters.*" By A. G. Perkin.

In a preliminary communication (*Proc.*, 1898, xiv., 56) it was shown that some phenolic colouring matters which dye mordanted fabrics decompose the alkaline acetates in presence of alcohol, forming mono-substituted salts. The present investigation indicates the general nature of this reaction in the case of colouring matters having hydroxyl radicles in relatively ortho-positions, although in the flavone groups some exceptions occur. In the following list of the salts prepared, those of calcium and barium have been formed by double decomposition from the alkali compounds. The colour and crystalline form are given only in the case of the potassium salt, and all were obtained crystalline unless otherwise stated.

Anthraquinone Group.—Potassium alizarine, $C_{14}H_7O_4K$, violet needles; sodium alizarine, $C_{14}H_7O_4Na$; barium alizarine, $(C_{14}H_7O_4)_2Ba$; calcium alizarine, $(C_{14}H_7O_4)_2Ca$, and potassium monobromalizarine, $C_{14}H_6BrO_4K$. Potassium anthragallol, $C_{14}H_7O_5K$, violet black needles;

also $C_{14}H_7O_5Na$; $(C_{14}H_7O_5)_2Ba$ (amorphous), and $(C_{14}H_7O_5)_2Ca$ (amorphous). Potassium purpurine, $C_{14}H_7O_5K$, and sodium purpurine, $C_{14}H_7O_5Na$, red needles. Potassium anthrapurpurine, $C_{14}H_7O_5K$, red needles. Other colouring matters of this group behave similarly, but quinizarine and metahydroxyanthraquinone do not give the reaction.

Flavone Group.—Morin yields the orange-yellow compounds, $C_{15}H_9O_7K$; $C_{15}H_9O_7Na$; $(C_{15}H_9O_7)_2Mg$; $(C_{15}H_9O_7)_2Ba$; $C_{15}H_5Br_4O_7K$; $C_{15}H_4Br_4O_7K_2$ (amorphous), and quercetin, $C_{15}H_9O_7K$; $C_{15}H_9O_7Na$; $(C_{15}H_9O_7)_2Ba$(?); $C_{15}H_7Br_2O_7K$, orange- coloured. Rhamnetin and rhamnazin are peculiar, and give respectively the salts $C_{16}H_{12}O_7$,$C_{16}H_{11}O_7K$ and $C_{17}H_{14}O_7$,$C_{17}H_{13}O_7K$. Potassium rutin, $C_{27}H_{31}O_{16}K$; potassium violaquercitrin, $C_{27}H_{25}O_{15}K$; potassium myrticolorin, $C_{27}H_{27}O_{16}K$, and potassium xanthorhamnin, $C_{28}H_{36}O_{17}$,$C_{28}H_{35}O_{17}K$(?), are yellow amorphous powders. Fisetin forms $C_{15}H_9O_6K$, yellow needles, and myricetin, $C_{15}H_{10}O_8$, and luteolin, $C_{15}H_{10}O_6$, behave similarly, the latter with production of very soluble salts. Apigenin, $C_{15}H_{10}O_5$, and chrysin, $C_{15}H_{10}O_4$, do not give the reaction.

In the *xanthone* group, gentisin and euxanthone do not yield salts in this manner, but galloflavin (Bohn and Graebe, *Ber.*, 1887. xx., 1329), a possible member, forms the salt, $C_{13}H_4O_9K_2$, described previously. Maclurin, $C_{13}H_{10}O_6$ (pentahydroxybenzophenone), gives a readily soluble compound, and alizarine yellow A (trihydroxybenzophenone) the salt $C_{13}H_9O_4K$. Cotoin and phloretin do not give the reaction.

Potassium and sodium hæmatein, $C_{16}H_{11}O_6K$, and $C_{16}H_{11}O_6Na$, are described, but compounds of brazilein, $C_{16}H_{12}O_5$, are too soluble for isolation. Santalin, $C_{15}H_{14}O_5$ (?), forms $C_{30}H_{27}O_{10}K$ (amorphous) and curcumin appears to form an analogous compound. From morin, quercetin, and alizarin, alkali salts are formed by boiling alcoholic potash, by carbonates, nitrites, succinates, lactates, benzoates, and salicylates in the presence of absolute alcohol, and by potassium acetate in the cold. Morin appears to form the compound $(C_{15}H_{10}O_7)_2,C_2O_4K_2$ with potassium oxalate. The salts of the anthraquinone group dissolve unchanged in boiling water; those of the flavone, xanthone, and benzophenone groups are decomposed, forming the colouring matter.

From potassium alizarine, $C_{14}H_7O_4K$, the ethers $C_{14}H_7O_3{\cdot}OMe$ and $C_{14}H_7O_3{\cdot}OEt$ are formed from the iodides at 230°. Ethylanthragallol, $C_{14}H_7O_4{\cdot}OEt$, was also obtained. These contain the alkyl group in the meta-position, have previously been prepared by Schunck and Marchlewski (*Trans.*, 1894. lxv., 185), and by Liebermann and Jellineck (*Ber.*, 1888, xxi., 1169), and indicate the position of the acidic hydroxyl.

Monomethyl purpurine, $C_{14}H_7O_4{\cdot}OMe$, evidently [OH : OCH_3 : OH = 1 : 2 : 4], forms red needles melting at 228—230°. Ethers of quercetin were not isolated in this manner, in consequence of accompanying decomposition.

To account for the acidic nature of these colouring matters, a change in the quinonoid form is suggested, capable of existence only in the form of a salt. Such a constitution has previously been proposed (*Trans.*, 1896, lxix., 1439) to explain the acid compounds of the flavone group, and a comparison of the *acid* and *basic* properties of these colouring matters reveals important points of resemblance.

Potassium alizarine, $C_{14}H_7O_4K$, is converted by cold acetic anhydride into *monacetylalizarin*, $C_{14}H_7O_4Ac$, crystallising in orange-yellow needles which melt at 198—201°; when allowed to remain some weeks with the reagent, diacetylalizarine is produced. Potassium-morin in the cold forms *tetracetylmorin*, $C_{15}H_6O_7Ac_4$, which crystallises in colourless prismatic needles, melts at 142—145°, and subsequently passes into a very soluble derivative. Potassium quercetin, $C_{15}H_9O_7K$, similarly gives *triacetylquercetin*, $C_{15}H_7O_7Ac_3$, melting at 167—169°, and quercetin sulphate, $C_{15}H_{10}O_7,H_2SO_4$, a *tetracetyl* compound which forms colourless needles melting at 193—194°.

The salts of morin and quercetin (Hlasiwetz and Pfaundler, *Jahresb.*, 1864, 560), of quercitrin (Liebermann and Hamburger, *Ber.*, 1879, xii., 1179), of fisetin (Schmid, *Ber.*, 1886, xix., 1739), and curcumin (Jackson and Menke, *J. Amer. Soc.*, 1882, iv., 77) appear to have been mixtures, as their percentage composition, though coinciding with the older formulæ of these colouring matters, does not agree with that required by their correct molecular weight.

41. "*Note on the Optical Activity of Gallotannic Acid.*" By Otto Rosenheim, Ph.D., and Philip Schidrowitz, Ph.D.

In a recent communication (*Trans.*, 1898, lxxiii., 878), the authors stated that the optical activity of gallotannic acid was first observed by F. M. Flawitzky, and that Günther independently re-discovered it in 1895, Flawitzky's communication remaining unnoticed. During the course of an investigation on the formation of gallic acid from gallotannic acid by the action of moulds, one of the authors (R.) has found that the merit of having first discovered the optical activity of the substance undoubtedly belongs to Ph. van Tieghem, who in a paper on "Fermentation du Tannin," says:—"Je me suis assuré que le tannin dévie vers la droite le plan de polarisation de la lumière incidente," and (*Ann. des Sciences Nat.*, 1867, [5], viii., 210) gives the specific rotation of the acid as $[\alpha]_D$ 16° +38·1°. This communication seems to have been unknown to Schiff, who six years later (*Annalen*, 1873, clxx., 75) devised the accepted gallotannic acid formula, and directly alluded to the "inactivity" of this substance, quoting F. W. Krecke's observations (*Arch. Néerl.*, 1871, vi., 193). It is remarkable that the important optical properties of this substance have been thrice discovered independently, and that until quite recently these have not become generally known and are not mentioned in any of the best known text- or hand-books. The fact that van Tieghem did not mention his discovery in a report on the subject (*Comptes Rendus*, 1867, lxv., 109), and that his original communication appeared in a botanical journal more or less inaccessible to chemists, may account in part for this omission.

CORRESPONDENCE.

ABSTRACTS OF CHEMICAL PAPERS.

To the Editor of the Chemical News

Sir,—Professor Stokes's letter on Chemical Abstracts has indicated clearly the disadvantages of the duplication of abstracts; his suggestion of co-operation of English-speaking nations is one which will commend itself favourably to the consideration of all who are interested in the advance of chemical science.

The scheme is one of considerable magnitude, and the details will require most careful consideration: I would draw attention to the fact that a needless duplication of abstracts occurs among our English Journals, and a consideration of how to avoid this must take place concurrently with, if not previous to, any discussion of Professor Stokes's proposition.

To illustrate my point, I will take those abstracts which come most under my notice—those on Analytical Chemistry; not infrequently I find abstracts, not only in your Journal, and in the *Analyst* (which is, in my opinion, the place where we should look for analytical abstracts), but in the *Journal of the Chemical Society*, the *Journal of the Society of Chemical Industry*, and sometimes in the *Journal of the Institute of Brewing*. Seeing that the size of our Journals shows a progressive increase, I can-

not but think that it would be a great advantage if the parent body, the Chemical Society, would call a conference of delegates from the various societies interested in chemistry (including naturally the Editors of the Journals) to consider the simplification of English abstracts, as well as the feasibility of the views put forward by Professor Stokes.—I am, &c.,

H. Droop Richmond.

Rodbourne, Claremont Road, St. Margarets, March 18, 1899.

NOTICES OF BOOKS.

The Microscopy of Drinking Water. By George Chandler Whipple. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1899. Pp. xii.-300. 8vo., 19 plates.

The author, who is Biologist and Director of Mt. Prospect Laboratory connected with the Department of Water Supply, Brooklyn, New York, and who had experience as Biologist of the Water Works at Boston, Massachusetts, has prepared this handsome volume with a twofold purpose. As he writes in the Preface, "It is intended primarily to serve as a guide to the water analyst and the water-works engineer, describing the methods of microscopical examination, assisting in the identification of the common microscopic organisms found in drinking water, and interpreting the results in the light of environmental studies. Its second purpose is to stimulate a greater interest in the study of microscopic aquatic life and general limnology from the practical and economic standpoint."

The subjects treated of in Part I. embrace methods of microscopical examination, its object, the organisms occurring in water from various sources (rain-, river,- and pond-water, canals, &c.); the physical properties of water (limnology); the geographical distribution of microscopic organisms, their seasonal distribution, as well as their horizontal and vertical distribution; the peculiar odours in water supplies, and their causes; the storage of surface water and of ground water; and the growth of organisms in reservoirs and water-pipes. The illustrations have been drawn chiefly from biological researches made at American localities, but the methods of examination, and to a large extent the aquatic life described, will prove equally valuable to investigators in Great Britain.

Part II. is devoted to descriptions of the most common organisms found in water supplies. In order to bring the matter within the scope of a practical and elementary survey, the descriptions are limited to the genera, no attempt being made to describe species and varieties.

A feature of the volume is the nineteen plates, the drawings having been made from photo-micrographs of living specimens, though some have been reproduced from standard publications. The Appendices contain useful tables and formulæ, and a bibliography of 483 entries. There is a well-made Index to the volume. The typography and paper do credit to the publishers.

H. C. B.

Practical Work in Physics. For Use in Schools and Colleges. By W. B. Wollacombe, M.A. (Oxon), B.Sc. (Lond.), Fellow of the Royal Astronomical and Physical Societies of London; Senior Science Master in King Edward's High School, Birmingham. Part IV.—Magnetism and Electricity, Oxford: at the Clarendon Press. 1899.

This modest little book is the fourth of the series of Practical Physics for Schools and Colleges; the previous issues have already been noticed in our columns, and we are glad to see that this last is quite up to the standard of excellence that has marked the others. The author's experience as a science master of long standing has enabled him to arrange the matter in the way most suited to the purpose in view, and the experiments described, though complete, are clear and simple. The apparatus needed is not costly, and most of it can be made by the pupil himself—a matter of very considerable value, as it gives him a clearer idea of the forces with which he is working than can be obtained when using the highly finished apparatus of the instrument maker, while at the same time there is a great saving in expense. Of the multitude of books for use in schools this series is certainly one of the best, and we are glad to learn that so far it has been favourably received.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 8, February 20, 1899.

Complex Oxides of the Rare Earths.—G. Wyrouboff and A. Verneuil.—Cerium possesses—in addition to the simple oxides, CeO, Ce_3O_4, and the peroxide obtained by the action of hydrogen peroxide on these oxides—the oxides Ce_3O_43CeO, and Ce_3O_4CeO; the first giving only non-condensed compounds, the second giving stable compounds only when CeO is replaced by one or other of the cerite or yttria earths. Ceroso-ceric oxide, whilst combining with lanthanum, didymium, and yttrium, forms complex oxides of the form Ce_3O_4MO, which polymerise with great facility and give two isomeric oxides, both condensed. In this state they form with acids, acid or neutral salts analogous to those of pure cerium. The discovery of these facts is of great importance in the separation of cerium from neighbouring metals. It follows that the methods used hitherto are perfectly irrational, and by a method shortly to be announced, depending on the above statements, cerium can be separated quantitatively, and consequently exactly estimated in the presence of any of the rare earths.

Action of Oxidising Agents on certain Amides.—Œschner de Coninck.—Not suitable for abstraction.

New Method of Preparation of Mixed Alcohol and Phenol Phosphoric Esters.—Albert Morel.—The author demonstrates the possibility of forming mixed phosphates by a method analogous to that for forming mixed carbonates, *i.e.*, by the reaction of alcoholates on triphenyl phosphate. A solution of $PO(OC_6H_5)_3$ in a mixture of absolute alcohol and anhydrous ether was treated successively with one, two, and three molecules of sodium ethylate dissolved in excess of absolute alcohol. The three products obtained were—

$$PO\langle^{OC_2H_5}_{(OC_6H_5)_2},\quad PO\langle^{(OC_2H_5)_2}_{OC_6H_5},\text{ and }PO\langle^{(OC_2H_6)_2}_{ONa}.$$

The triethyl phosphate was not obtained by this method, which is probably accounted for by the dissimilarity existing between one of the hydroxyls of phosphoric acid and the other two. Conversely, triethylphosphate, treated with water, gives the stable diethylphosphoric acid,—

$$PO\langle^{OH}_{(OC_2H_5)_2}.$$

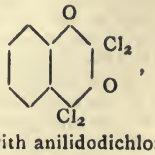
Action of the Amyl Alcohol of Fermentation on its Sodium Derivative.—M. Guerbet.—The author has isolated three products of the reaction ensuing when amyl alcohol is warmed with sodium, *viz.*, an alcohol, $C_{10}H_{22}O$; an acid, $C_{10}H_{20}O_2$; and isovaleric acid. The formation of these bodies may be expressed as follows:—

(1). $C_5H_{11}NaO+2C_5H_{12}O=C_{10}H_{22}O+C_5H_9NaO_2+4H$:

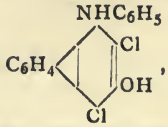
(2). $C_{10}H_{20}O+NaOH=C_{10}H_{19}NaO_2+4H$.

Liebig's Annalen der Chemie,
Vol. ccc., March 9, 1898.

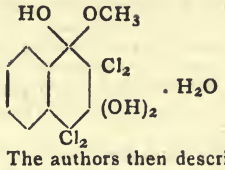
On 2.4-Tetrachloro-1.3-dicetotetrahydronaphthalene.—Th. Zincke and G. Egly.—To obtain the 1.3.2.4-(meta) derivatives,—



the authors started with anilidodichloronaphthol β,—



which they treated with chlorine. But since then naphtharesorcine, or 1.3-dioxynaphthalene, has been discovered, and this substance is found to be much better for the preparation of the *m*-diacetotetrachloride. Chlorine is passed through a solution of naphtharesorcine in ten parts of acetic acid until saturation. After twenty-four hours, this is evaporated down, and the residue treated with water and a little hydrochloric acid. The hydrate of the dicetachloride, $C_{10}H_4Cl_4O_2.3H_2O$, is then deposited in flattened needles, which are purified by crystallisation in warm benzene. The anhydrous dicetochloride crystallises in boiling benzene in prisms, generally arranged in groups or stars. If the hydrate of the dicetochloride is boiled with methanol in a flask fitted with a vertical condenser, and the excess of this latter then driven off by evaporation, a syrupy product remains which, when crystallised in hot benzene, forms needles fusible at 156°; it is the methylate, to which the constitution—



has been given. The authors then describe the action of Na_2CO_3 on the dicetatetrachloride, of Cl_2CaO on the *m*-dicetatetrachloride represented by the equation $C_{10}H_4Cl_4O_2 + ClOH = C_{10}H_5Cl_5O_2$, and of KOH on pentachloracetonic acid.

Carbonates of the Dioxybenzenes.—A. Einhorn.—Having observed that, when concentrating an alcoholic solution of carbonate of pyrocatechin by heat, this compound is converted into an oxethyl-derivative, the author turned his attention to the amines, and found that these, and especially the secondary amines, lead very easily to derivatives of the formula $C_6H_4<^{OCONRR'}_{OH}$. He then extended his researches to the carbonates of the other dioxybenzenes. A number of these, such as ethyl carbonate of pyrocatechin, amylcarbonate of pyrocatechin, phenylhydrazide, &c., and their properties are then described. To obtain carbonate of resorcine free from chlorine, it is necessary to react with 25 grms. of phosgene dissolved in toluene on 30 grms. of resorcine dissolved in 250 grms. of pyridine at 0° while constantly agitating. After half an hour, the whole is poured into water and the carbonate is precipitated; it is in the form of an amorphous powder, fusible at 190°, and has not yet been crystallised. The action of piperidine on this carbonate gives two products, the piperidide, $C_6H_4(OH)_m.O.CO.NC_5H_{10}$, which is soluble, and the dipiperidide, $C_6H_4(OCO.NC_5H_{10})^1_2$, which is insoluble.

Reduction of Benzylamine-carbonic Acids.—A. Einhorn and J. Brantl.—The most interesting of these denitrated products is the *o*-oxymethylhexahydrobenzoic acid. It is without doubt formed by the splitting up of the cis-hexahydro-*o*-diethylbenzylaminecarbonic acid into diethylamine and hexahydrophthalide, $C_6H_{10}<^{CH_2}_{CO}>O$, and the subsequent hydratation of this latter, which is lactone.

Dimethylaniline-phthaloylic Acid.—H. Limpricht.—This acid, of which the formula is—

$$C_6H_4<^{CO—C_6H_4N(CH_3)_2}_{COOH},$$

is produced by the action of 40 grms. of $AlCl_3$ on a mixture of 45 grms. of phthalic anhydride, 37 grms. of dimethylaniline, and 200 grms. of bisulphide of carbon; the chloride of aluminium must be added a little at a time as it causes a rise of temperature. The residue, after boiling and distillation, is dissolved in dilute warm hydrochloric acid, the phthaloylic acid is deposited on cooling in the form of yellow crystals fusible at 205°, and soluble in alcohol, acetone, and benzene, slightly in ether, very slightly in CS_2, and not at all in water. When submitted to a prolonged reduction by NH_3 and zinc at about 80°, phthaloylic acid gives rise to a hydro-derivative—

$$C_6H_4<^{CH_2C_6H_4N(CH_3)_2}_{CO_2H}.$$

The Action of Chloride of Tetrazodiphenyl on Acetylacetic Acid and on the Phenylhydrazone of Benzylic Aldehyde.—E. Wedekind.—Twenty grms. of acetylacetic ether were saponified by 10 grms. of KHO with 345 c.c. of water. After cooling with ice, a solution of tetrazoic chloride (obtained from 28·5 grms. of benzidine) was added. The dark brown product was then washed with water, dried, and exhausted with boiling chloroform. By adding ligroïn to the concentrated chloroformic solution, the cyclocetone is separated in the form of a reddish brown amorphous powder, slightly soluble in the ordinary solvents, and soluble in H_2SO_4 with a green colour; by adding water it is re precipitated unchanged. Sulphide of ammonium reduces cycloformazylcetone, giving a compound crystallising in boiling chloroform in brownish prisms melting at 145—148°. The action of phenylhydrazin gives a brown body melting at 180—185°, from which an orange compound is extracted by soda; the crystals are fusible at 197°, and dissolve in sulphuric acid, giving a crimson colour.

MEETINGS FOR THE WEEK.

WEDNESDAY, 29th.—Institution of Mining and Metallurgy, 6.30. Annual General Meeting.
— Chemical, 3. Anniversary Meeting. Election of Officers and Council. President's Address.

Chemist wanted for large Works in North of England. Preference given to one well up in Iron, Steel, and Fuel Analysis.—Apply, giving full particulars and salary required, to "Iron," CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, an Analytical Chemist for Mines in Central America.—Reply, Santa Francisca Gold Mines, Ltd., London and South Western Bank Buildings, Small Street, Bristol.

Wanted, an Analytical Chemist of exceptionally high and proved ability and accuracy, with good experience in testing Medicinal Chemicals, to take up the position of Chief Analyst at the Works of a leading London Firm of Manufacturing Chemists. A gentleman who has taken University Degrees preferred.—Address, stating age, qualifications, and experience, to "Analyst," care of Messrs. Markby, Stewart, and Co., Solicitors, 57, Coleman Street, London, E.C.

TO INVENTORS AND EXPERIMENTALISTS.

Laboratories specially fitted up for Experimental and Analytical work can be hired in Westminster at reasonable prices. Arrangements also made for placing inventions on the market.—Apply to L. W., CHEMICAL NEWS Office, 6 and 7, Creed Lane, Ludgate Hill, London, E.C.

Analytical Laboratory, fitted for Bacteriological Work, For Sale; in good position; low rent; no reasonable offer refused.—Apply, Baird and Tatlock, 14, Cross Street, Hatton Garden, E.C.

THE CHEMICAL NEWS.

Vol. LXXIX., No. 2053.

ON THE ORDER OF APPEARANCE OF CHEMICAL SUBSTANCES AT DIFFERENT STELLAR TEMPERATURES.*

By Sir NORMAN LOCKYER, K.C.B., F.R.S.

In a paper on the "Chemistry of the Hottest Stars," in 1897 (*Roy. Soc. Proc.*, vol. lxi., p. 148), I stated the results so far arrived at concerning the order in which certain spectral lines appeared and others disappeared in stars arranged in a series of ascending temperatures. Since that paper was written many important advances have been made, so that I have been able in the meantime to considerably extend the research. Among these advances I may mention the following:—

1. With regard to the metals, my recent note on the enhanced lines in the spectrum of α Cygni (*Supra*, p. 320) enables us to deal with the lines observed at the highest temperature in the spectra of the following substances:—Fe, Mg, Ca, Sr, V, Ti, Ni, Mn, Cr, and Cu.

The temperature ranges of the enhanced lines of these metals have been investigated with the following results:—

Table I.

Metal.	Range of temperature (upward series).	Range of temperature (downward series).
Mg ..	α Ursæ Min. to γ Argus	α Eridani to Procyon.
Ca ..	α Tauri to γ Agrus	α Eridani to Arcturus.
Fe ..	α Tauri to ζ Tauri	β Persei to Arcturus.
Ti ..	α Tauri to ζ Tauri	β Persei to Arcturus.
Cu ..	α Ursæ Min. to α Cygni	β Persei to Procyon.
Mn ..	α Ursæ Min. to α Cygni	β Persei to Procyon.
Ni ..	α Ursæ Min. to α Cygni	β Persei to Procyon.
Cr ..	α Ursæ Min. to α Cygni	γ Lyræ to Procyon.
V ..	α Ursæ Min. to α Cygni	Sirius to Procyon.
Sr ..	α Tauri to α Cygni	Sirius to Arcturus.

I pointed out in the note referred to that the enhanced lines of the above substances seemed to account for almost all of the more marked lines in α Cygni. It is on this ground that I have investigated their behaviour in other stars before waiting for the results of the complete inquiry. Another reason has been that although in addition to the enhanced lines of the metals shown in the foregoing table, those of—

Ba, Cd, Mo, La, Sb, Pd, Ta, Rh, Er

and—

Yt, Ce, Wo, U, Zr, Pb, Co, Bi,

have already been investigated with lower dispersion, and a spark obtained with the use of a much less jar capacity, so far I have no certainty that any of these substances exist in the reversing layers of stars of intermediate temperature.

2. The temperature ranges of the arc lines of some of the metals have also been investigated, and the results are shown in the following table:—

Table II.

Metal.	Range of temperature (upward series).	Range of temperature (downward series).
Fe ..	α Tauri to α Cygni	α Canis Majoris to Arcturus.
Ca ..	α Tauri to α Ursæ Min.	α Canis Majoris to Arcturus.
Mn ..	α Tauri to α Ursæ Min.	α Canis Majoris to Arcturus.

* A Paper read before the Royal Society, February 23, 1899.

3. The new series of lines discovered by Professor Pickering, and described by him as representing a new form of hydrogen (*Astro. Phys. Journ.*, 1897, vol. v., p. 92), has been found in the spectra of ζ, ε, δ, and κ Orionis photographed at Kensington in 1892, and Mr. McClean has traced the lines in γ Argus.

We are therefore now in a better position to determine the relation of this new gas to other gases, both known and unknown, appearing in stars of nearly equal temperature.

4. In addition to the unknown lines at $\lambda\lambda$ 4089·2 and 4649·2, referred to in my last communication on this subject (*Roy. Soc. Proc.*, vol. lxii., p. 52), three other unknown lines occur in γ Argus.

As these most probably reveal still undiscovered gases, I include them in Table III., showing the limits of stellar temperature to which the various known and unknown lines, probably of gaseous origins, extend.

5. Mr. McClean has stated that certain of the oxygen lines (amongst which is the strong triplet at $\lambda\lambda$ 4070·1, 4072·4, and 4076·3) appear in the spectrum of β Crucis and other stars of nearly equal temperature. My own observations, so far as they have gone, tend to confirm this view, but other photographs and more laboratory work are needed to explain certain changes of intensity which have been observed. The lines attributed by Mr. McClean to oxygen have been noted between α Crucis and ζ Orionis in the upward series, and in stars at about the α Eridani stage of temperature in the downward series.

6. There is evidence that the strongest lines of nitrogen at λ 3995·2 and λ 4630·9 make their appearance in stars at about the temperature of α Crucis. These lines appear from Rigel to ζ Orionis in the upward series, and are present in stars at the α Eridani stage in the downward.

7. I pointed out many years ago (*Roy. Soc. Proc.*, vol. xxx., p. 461) that at high temperatures the flutings of carbon in the violet are replaced by a line at λ 4267·5. There is a line at this wave-length in the spectra of stars ranging in temperature from that of Rigel to ζ Orionis on the up side, and from α Eridani to β Persei on the down side, of the temperature curve.

There is no known line of gases or metals to which this line can be assigned. It is probable therefore that carbon exists in stars of the same temperature as that at which oxygen and nitrogen have been traced.

8. Two lines in the spectrum of silicium (λ 4128·5 and λ 4131·5) have been traced in stars between the temperatures of α Ursæ Min. and α Crucis in the upward series, and between those of α Eridani and Procyon in the downward.

The accompanying map shows the facts relating to stars as hot as, or hotter than, the sun, as we know them at present.

Description of Map.

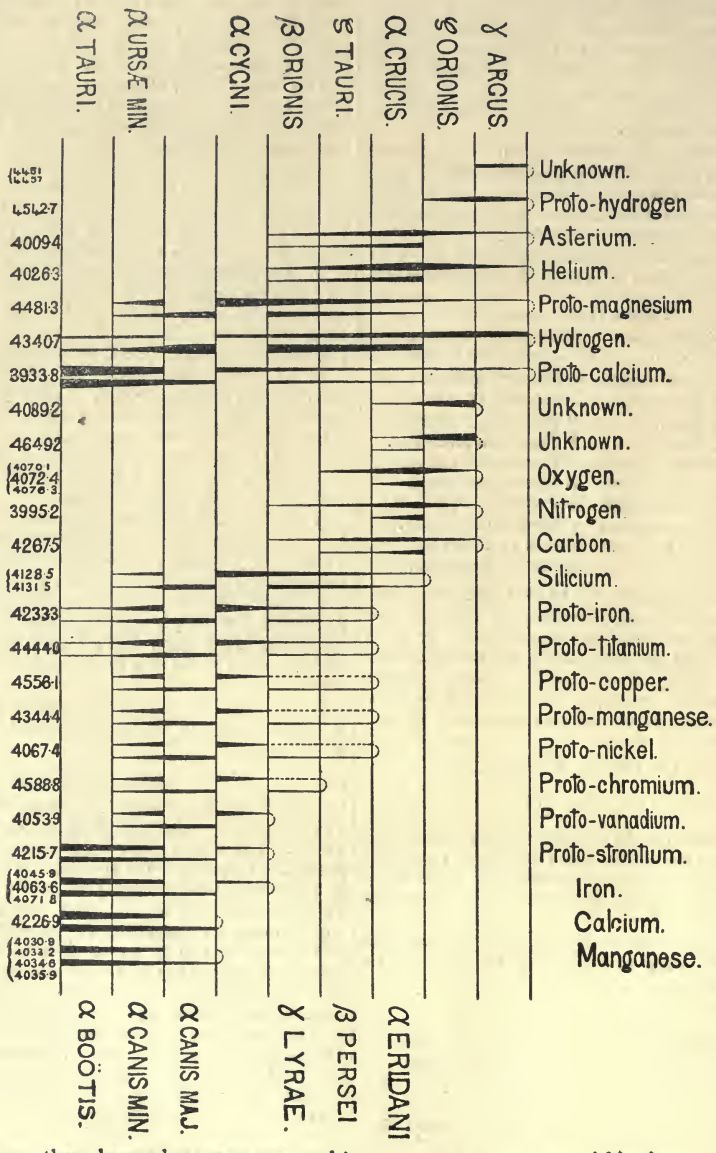
The map is arranged on the following plan:—The temperature of the sun and Arcturus forms the lowest stage. The upper limit is defined by γ Argus, the hottest star so far known. On the left the stars named are those of increasing temperature; on the right those of decreasing temperature. Those on the same horizon represent equal mean temperature so far as the cleveite gas and enhanced lines help us to determine them. The blank spaces indicate that so far no star has been photographed in the spectrum of which the enhanced lines exactly match those on the opposite side.

The names of the various chemical substances included in the discussion are given at the top. I have retained the prefix "proto" to that condition of each metallic vapour which gives us the enhanced lines alone, and I have added it to that form of hydrogen seen only in the hottest stars.

The behaviour of the most typical line of each chemical substance is indicated by a double line looped at the top at its highest range. The length and varying thickness of the lines in stars on both sides of the temperature

TABLE III.

Origin.	λ of chief lines.	Range in ascending series of stars.	Range in descending series of stars.
Unknown	4457 4451 3876	Seen only in γ Argus.	
Hydrogen (new) ..	4544·0 4200·4	ζ Orionis to γ Argus	No stars available.
Unknown	4089·2	α Crucis to ζ Orionis	
,, ...	4649·2	,, ,,	α Eridani.
Helium	4471·6 4026·3	Rigel to γ Argus	α Eridani to γ Lyræ.
Asterium	4388 4009	,, ,,	α Eridani to γ Lyræ.
Hydrogen	Complete series	Aldebaran to γ Argus	α Eridani to Arcturus.



curve are derived from the observed appearance and intensity of the lines, noted in the different stars.

The wave-lengths of the lines discussed are shown at the bottom of the map.

Addendum.

The facts embodied in the map present to us the spectral changes noted in stars of Groups III., IV., and V., of my classification (*Roy. Soc. Proc.*, 1887, vol. xliii.,

p. 117), and are a result of a more general inquiry than those referred to in my previous papers (*Roy. Soc. Proc.*, 1888, vol. xliv., p. 1; *Roy. Soc. Proc.*, 1889, vol. xlv., p. 380; *Phil. Trans.*, A., 1893, vol. clxxxiv., p. 725), the origins of a very considerable number of stellar lines having since then been traced to enhanced lines of metals and to known gases.

It will be seen that this more general inquiry entirely justifies the prior statement (*Roy. Soc. Proc.*, vol. lxi., p. 182), that the metallic lines are thickest in stars increasing their temperatures, and that the hydrogen lines are thickest in stars decreasing their temperatures; in other words, on the opposite arms of the temperature curve. I have already stated a possible explanation (*Roy. Soc. Proc.*, vol. lxi., p. 183).

It will be observed that, so far, I have not been able to find stellar spectra on the downward side corresponding to those of γ Argus and ζ Orionis; but it is more than probable that near the apex of the curve only a small change will be observed; their default, therefore, is of less consequence than it might have been.

The same remark applies to α Cygni and Sirius; but here it is certain that the differences in the relative intensities of the gaseous and enhanced lines will be considerable, judging from what happens above and below the heat stages represented by them.

The stars used in the discussion give us very definite results, showing that the various chemical forms are introduced at six very distinct heat levels.

I next proceed to make some remarks upon the series of facts now for the first time brought together; it must, however, be borne in mind that all the chemical elements and all parts of the spectrum have not yet been included in the survey.

1. Hydrogen appears throughout both series of stars from top to bottom. Proto-magnesium and proto-calcium follow suit very nearly; but the highest intensity of the former is reached at the stage represented by α Cygni, and of the latter at the solar temperature represented by α Tauri and Arcturus.
2. With the above exceptions, all the chemical forms so far traced are relatively short-lived.

This is the first important differentiation. In the light of (1) we are justified in assuming that the substances in (2) would be visible in the stellar reversing layers if they were there.

3. In the stars of higher temperatures we deal generally with gases. Below the stages represented by β Orionis and γ Lyræ we deal with proto-metals and metals, hydrogen being the only exception.
4. The proto-metals make their appearance at about the same heat-level at which the gases (with carbon), always excepting hydrogen, begin to die out.

This is the second important differentiation. It is interesting to notice the distinct difference of behaviour of carbon and silicium in the descending series; the former goes through the same stages as oxygen and nitrogen, the latter behaves like the proto-metals.

5. With the exception of iron the metals, as contra-distinguished from the proto-metals, only make their appearance in stars at and below the heat-level of Sirius.

This is the third important differentiation. It is accompanied with a notable *diminution* of hydrogen and proto-magnesium, and with an *increase* of proto-calcium: indeed the latter seems generally to vary inversely with the hydrogen.

In all these changes we seem to be brought into presence of successive polymerisation due to reduction of temperature. Of the origin of proto-magnesium and proto-calcium the stars as yet tell us nothing, but it is difficult to believe that the earliest forms of the other metals are not built up of some of the constituents of the heat ranges represented by those between γ Argus and α Crucis.

The question arises whether the order of visibility at reduced temperatures now indicated does not explain the absence of proto-hydrogen, oxygen, and nitrogen from the spectra of the sun and nebulæ, the metals present in, and the absence of quartz from, meteorites, and the similarity of the gaseous products obtained from them and metals, native and other, in vacuo at high temperatures.

I have finally to express my obligations to those who have aided me in the present inquiry. For some of the metals used I am indebted to Mr. George Matthey, F.R.S., who has kindly placed the resources of his establishment so entirely at my disposal that I feel it is impossible to thank him sufficiently. For the determination of wave-lengths and the correspondence of terrestrial and stellar lines, Mr. Baxandall is responsible, while Mr. Fowler has assisted in the determination of the various stellar groups. The photographs of the enhanced lines obtained by the use of the Spottiswoode coil have been taken by Mr. Butler. The actual construction of the map from the available photographs has devolved upon Mr. Baxandall, Dr. Lockyer co-operating in the case of stars of the highest temperature.

NOTES ON THE ELECTRO-DEPOSITION OF VANADIUM.*

By SHERARD COWPER-COLES, M.Inst.M.M.

VANADIUM has not received the attention it deserves at the hands of electro-metallurgists. Vanadium oxidises slowly in the air, and has a very high melting point, about 2000° C. (equal to 3600° F.), and is neither volatile nor fusible when heated to redness in hydrogen. Vanadium is widely distributed (see "Mineral Industry," vol. vi.), but it is not often found in large quantities. It was first discovered by Seftström in 1830, in the iron obtained from the Taberg ores.

The metal is not readily attacked by hydrochloric acid, either when hot or cold, neither strong nor dilute sulphuric acid act upon the metal in the cold, but when heated with strong acid the metal slowly dissolves, giving a greyish-yellow solution. Both hot and cold solutions of caustic soda are without action on the metal, but when fused with the hydroxide, hydrogen is evolved, and vanadate formed. Nitric acid of all strength oxidises the metal with violence, evolving nitrous fumes and forming a blue liquid. The specific gravity of vanadium at 50° F. is 5·5, being somewhat lighter than zinc, and about twice as heavy as aluminium.

Metallic vanadium made by reduction from the dichloride in hydrogen, is a light whitish-grey coloured powder, which under the microscope reflects light most powerfully, and appears as a brilliant crystalline mass, possessing a silver-white lustre (Roscoe and Schorlemmer's "Treatise on Chemistry."

Vanadium was originally found in Mexico. Recently it has been discovered in considerable quantities near Santa Márta in Spain. In the Spanish mines, it is found associated with lead, tellurium, gold, and silver. Some of the ore contains as much as 124 lbs. of metallic vanadium to the ton.

Vanadium has also been mined on the elevated plains of the Great Chain of the Andes, where anthracite mines exist, containing two parallel inclined beds of vanadium-containing coal, from 2 to 3 metres thick and 1004 metres long. It is also found in Peru, in certain anthracite coals, which, according to analysis, contain about 4·5 per cent.

An interesting paper has recently been read before the Geological Society of Washington by Mr. W. F. Hille-

* A Paper read before the Institution of Mining and Metallurgy, March 15th, 1899.

brand, on the distribution and quantitative occurrence of vanadium in the rocks of the United States.

Gore has endeavoured to deposit vanadium from aqueous solutions, but with unsatisfactory results. The electrolyte employed by him was one composed of vanadic acid, dissolved in pure dilute hydrochloric acid by means of an electric current, using a retort carbon anode and a platinum cathode; the gas set free at the anode was observed to have a smell of ozone. He also tried a solution of dilute sulphuric acid with pure vanadate of ammonia, and electrolysed the solution with platinum electrodes. The electrolyte turned a bluish-black colour at the cathode, and a jet-black powder of some thickness was deposited upon it.

Schicht dissolved vanadium chloride in water containing hydrochloric acid, and electrolysed the solution. Inert deposition took place in the blue liquid, the vanadium acid being merely reduced to oxide.

The author has succeeded in obtaining brilliant metallic deposits of vanadium, the colour being almost as white as that of silver, from a solution prepared as follows:—

The vanadic anhydride, V_2O_5, was boiled with an excess of caustic soda, the sodium vanadate thus formed being decomposed by an excess of hydrochloric acid. The proportions were as follows:—1·75 parts of vanadic anhydride (equal to 1 oz. per gallon of solution) were dissolved in 2 parts of caustic soda and 160 parts of water, to which 32 parts of hydrochloric acid was afterwards added.

The best results were obtained with a current density of 18 to 20 ampères per sq. ft., the E.M.F. at the terminals of the electrolysing cell being 1·88. The solution was worked at a temperature of about 180° F. If higher or lower current densities were used red-brown oxide was deposited along with the metallic vanadium. A reddish-brown non-adherent powder was deposited from cold solutions at the same current density. The solution when first made up was of a light greenish-yellow colour. After boiling with a carbon anode for some time it became darker, and after passing a current it turned a rich dark green, after a good deal of metal had been taken from the solution it appeared bluish. When a solution containing 2 oz. of vanadium to the gallon was electrolysed the deposit was not so white as that obtained from a solution containing 1 oz., the deposit having a steely appearance.

Vanadium is found to increase the tensile strength of iron, copper, and aluminium when added to those metals, also the ductility. The present use of the metal is almost exclusively confined to converting aniline into fixed black dyes for indelible ink, and the colouring of glass.

The present price of vanadium oxide is about £2 per pound. Sir Henry Roscoe some years ago produced a few grms. of metallic vanadium; now that the author has shown that it can be readily electro-deposited in a metallic form, it is to be hoped that new uses will be found for this interesting metal.

ON CRUCIBLE STEEL CASTINGS.

By SERGIUS KERN, M.E., St. Petersburg.

MANY difficulties arise when casting hollow steel castings having a thin body,—for instance $\frac{3}{8}$" to $\frac{1}{2}$" in thickness,—especially when the rules for delivery prescribe testing the hollow castings under pressure of steam or water.

When using ordinary carbon steel, notwithstanding the usual top-heads placed on the pattern, in places where thin parts of the casting adjoin thicker places, very often the usual local flaws are discovered; when water pressure is applied, in these places the water passes in the form of fountains, drops, or mist, according to the sizes of the local flaws or cavities in the metal. Frequently chasing the metal in these places, by hand hammers, arrests the permeability of the casting; but often this is of no use, and castings are rejected.

I make my castings by using a coke crucible furnace containing four crucibles with a charge of two-thirds of a cwt. in each pot. The carbon steel castings contain on the average:—

Carbon	0·38 per cent.
Manganese	0·42 ,,
Silicon	0·33 ,,
Phosphorus	0·06 ,,
Sulphur	

The mixture for crucible steel melting is composed of 80 per cent of punchings, coming from the punchings of soft steel ship-plates, and 20 per cent of very soft puddled iron, containing about 0·06 per cent of carbon and 0·03 per cent of manganese. Before casting, into each crucible some $\frac{3}{4}$ of a pound of silico-spiegel is introduced, containing 10 per cent of silicon and 15 per cent of manganese. Next, into every crucible taken out from the furnace, and ready for casting, 25 grms. of aluminium are thrown.

At present I apply such a system only for small castings used in ship-building; all the hollow castings intended for keeping water or steam under pressure, in actual service, are made from nickel steel.

I found, as other metallurgists have done also, that in order to get a dense steel casting in which the local flaws or contractions are brought to a minimum, the best thing is to introduce 2 per cent of nickel into the steel castings. I proceed as follows:—The crucible charge consists of 73 per cent of punchings, 25 per cent of puddled iron, and 2 per cent of nickel, sold in the form of small cubes. When melted, $\frac{3}{4}$ of a pound of silico-spiegel and 45 grms. of 80 per cent ferromanganese, are thrown into each crucible, by a funnel, and the metal is left to stand for twenty minutes in the furnace. When taken out for casting, after this lapse of time, the crucibles are cleaned from slag, and 25 grms. of aluminium are thrown into every pot.

Tests of such steel ordinarily give about 38 tons per square inch of breaking strain and 12 per cent of elongation in a length of 2 inches.

March 16, 1899.

NOTE ON THE ATOMIC WEIGHTS OF PRASEODYMIUM AND NEODYMIUM.

By HARRY C. JONES.

THE recent article by Carl von Schele (*Zeit. Anorg. Chim.*, 1898, xvii., 310), on the atomic weight of praseodymium, records the third piece of work which was done on the same problem in the last year or two. Brauner (*Proc. Chem. Soc.*, 1898, No. 191, p. 70) published the results of his determinations of the atomic weights of praseodymium and neodymium in April last, while my own results (*Amer. Chem. Journ.*, 1898, xx., 345) were published in May.

The object of this note is to call attention to the agreement between the values found by the three experimenters, working simultaneously, but entirely independently, and to the difference between their results and those of von Welsbach (*Monatsh.*, 1885, vi., 477), which were the only determinations on record a year ago. The work of von Welsbach dates from 1885, when he separated the supposed element didymium into the two constituents praseodymium and neodymium.

Brauner and myself obtained our material from Mr. Waldron Shapleigh, of the Welsbach Light Company, Gloucester, New Jersey, U.S.A. Schele, on the other hand, prepared his material from monazite furnished by Clève. The source of the material was thus not the same in all three cases.

After further purifying his material, Brauner determined the atomic weight of praseodymium by analysing the oxalate and synthesising the sulphate, and obtained as a mean of thirteen values 140·95, varying between 140·84 and 141·19. He obtained the value 143·63 for neodymium.

Schele, working with praseodymium oxide which he had very carefully purified, synthesised the sulphate, and found the atomic weight of praseodymium to be 140·4, as the average of five determinations which varied from 140·30 to 140·46.

The present writer also further purified the material furnished by Shapleigh until an analysis by Rowland's large spectroscope showed that it was fairly pure. The amount of praseodymium in the neodymium, and of neodymium in the praseodymium, was then determined by means of the intensity of the absorption bands. The oxalates of praseodymium and neodymium were then converted into the oxides. The superoxide of praseodymium was reduced in a stream of hydrogen to the sesquioxide, and from the sesquioxides the sulphates were synthesised.

The atomic weight of praseodymium was found to be 140·45, with a maximum-minimum difference in ten determinations of 0·16.

The mean of ten determinations of the atomic weight of neodymium was 143·6, with the same maximum-minimum difference as above.

The agreement between the three series of results will be seen best by glancing at the following table, which will also show how widely they differ from the results of von Welsbach.

	von Welsbach.	Brauner.	von Schele.	H. C. Jones.
At. wt. Pr. ..	143·6	140·95	140·4	140·45
,, Nd. ..	140·8	143·63	—	143·6

The agreement between my own value for the atomic weight of praseodymium and that found by von Schele is very close, while Brauner's value here is a little higher. The atomic weight of neodymium, on the other hand, as found by Brauner and myself, is almost exactly the same. By comparing these three values with those of von Welsbach, it will be seen that they agree much more closely with the results of von Welsbach if the latter are interchanged. The atomic weight of praseodymium found by von Schele and myself is a little lower than von Welsbach's atomic weight of neodymium, but the atomic weight of neodymium as found by Brauner and myself is identical with von Welsbach's atomic weight of praseodymium. These three pieces of work, then, make it quite certain that the original determinations of von Welsbach are not free from error, and, indeed, they were published as only tentative, and not described in any detail.

It is a striking coincidence that a problem which remained untouched since 1885 should have been taken up at the same time by three indiviuals as widely removed as Prague, Upsala, and Baltimore.

Chemical Laboratory, Johns Hopkins University,
November, 1898.

THE

USE OF THE TRANSITION TEMPERATURES OF COMPLEX SYSTEMS AS FIXED POINTS IN THERMOMETRY.*

By THEODORE WILLIAM RICHARDS and JESSE BRIGGS CHURCHILL.

In a brief paper upon the transition temperature of sodic sulphate (*Am. Journ. Sci.*, 1898, vi., 201; also *Zeitschr. Phys. Chem.*, xxvi., 690), we have recently shown that this non-variant point is capable of being reproduced in practice with great certainty, and that it is therefore admirably suited for use as a standard of reference in thermometry. We pointed out the fact that many other systems composed of two or more components might answer equally well, and declared our intention of fixing as many points as possible in order to simplify the accurate measurement of temperature. The subsequent appearance of a hastily written note by Messrs. Meyerhoffer and Saunders (*Zeitschr. Phys. Chem.*, October, 1898, xxvii., 367), claiming for themselves a part of this scheme, has prompted the present paper, which has as its object a more detailed statement of the plan.

It is obvious that, while any number of components might be employed simultaneously for this service, the simpler systems will be on the whole the most useful. Water is so omnipresent as to be difficult to exclude from any kind of experiment; hence the investigator is almost forced to adopt it as one of the components. The choice is then of the other material or materials, and the first step was obviously to study all common substances with a view to discover the probable usefulness of the transition temperatures of their aqueous crystals. If a complete temperature scale could not be built up from such simple data it would obviously become necessary to investigate quintuple points, of which a very great number could be devised. This additional complication could not but be regretted, however; for it involves the necessity of preparing two salts instead of one in a pure state, it renders less easy the use of the same material over and over again, and it introduces a complication which might seriously retard the speed of attaining equilibrium, and hence the constancy of the desired point.

After studying with care the published records of all the field of inorganic chemistry, about two dozen salts were selected as probably suitable for the work in hand. Of these magnesic and nickelous sulphates, calcic and nickelous nitrates, nickelous chloride, and borax were rejected as being too inconstant in their indications. The lack of constancy was due sometimes to the smallness of the latent heat of transition, and sometimes to a superabundance of crystalline hydrates. On the other hand, at least eight of the new salts gave results comparable in certainty with those given by the ever trustworthy Glauber's salt. These salts are given in the the table below:—

Transition Temperatures of Nine Salts.

Salt.	By mercury thermometer.	By hydrogen thermometer.
Sodic chromate, $Na_2CrO_4.10H_2O$ ..	19·93	19·85
Sodic sulphate, $Na_2SO_4.10H_2O$ ..	32·484	32·379
Sodic carbonate, $Na_2CO_3.10H_2O$ ..	35·2	35·1
Sodic thiosulphate, $Na_2S_2O_3.5H_2O$ ..	48·1	48·0
Sodic bromide, $NaBr.2H_2O$	50·8	50·7
Manganous chloride, $MnCl_2.4H_2O$ ..	57·9	57·8
Strontic chloride, $SrCl.6H_2O$	61·1	61·0
Sodic phosphate, $Na_3PO_4.12H_2O$ ..	73·5	73·4
Baric hydroxide, $Ba(OH)_2.8H_2O$ ..	78·0	77·9

The temperatures given above are only approximations, and are subject to future revision; at this stage of the work our effort has been only to determine if the points were constant, and not to fix their absolute value. Besides these nine, several other salts promise well. Baric hydrate, given above, was our first trial of three components, for the carbonate was naturally allowed to be present. The study of such quintuple points has now been interrupted by Messrs. Meyerhoffer and Saunders's claim.

These gentlemen studied in a very hasty fashion the transition temperature of Glauber's salt in the presence of an excess of common salt. Although theoretically sound, such a system labours under a serious practical disadvantage; for the addition of heat to it means the dissolving of common salt as well as the melting of crystallised sodic sulphate and the depositing of anhydrous material. The first of these processes is obviously less speedy than the others, and must surely occupy appreciable time even if the solid is finely powdered. Such a "lag" inevitably

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No. 10, January, 1899.

affects the temperature; our own experience with this mixture as well as with other similar ones supports this inference, and is anything but reassuring. Indeed, we found that Glauber's salt itself did not give absolutely accurate results if it were allowed to "freeze" instead of to "melt," for a similar reason.

We agree with Messrs. Meyerhoffer and Saunders as to the great desirability of uniting upon some normal temperature for the graduating of flasks, &c., but we cannot conclude with them that 18° is the best temperature. In America the steam-heated winters and sun-heated summers raise the average temperature of our laboratories at least to 20°, and indeed this temperature is more comfortable than 18° unless one is performing active manual labour. Hence at Harvard we have settled upon 20° as the normal room temperature. Sodic chromate (19·85) clearly gives us very nearly the standard of reference which we desire. In determining the specific gravities of liquids, a temperature *above* that of the room is preferable to one *below*—for the expansion of the liquid during the drying of the exterior of the pycnometer is otherwise apt to be troublesome, hence 18° is not suitable for this purpose. The authors before mentioned suggest the use of a bath of mixed salts as a means of keeping the temperature constant during determinations of electrolytic conductivity; but it should be pointed out that in such work the neighbourhood of a very large amount of a good electrolyte is necessarily risky, except in the best of hands. This is especially the case when the substance effloresces to form a fine powder, easily wafted around by currents of air. In short, while for some work with closed vessels demanding the greatest accuracy such a bath may be invaluable, the Ostwald thermostat is the safest and most convenient appliance for preserving a constant temperature in the laboratory. The baths of "melting" crystals will find their greatest use in the standardising of thermometers at fixed points; and these thermometers will continue to serve as the most handy means of attaining and registering any desired temperature. It is obvious that if a thermometer is standardised under exactly the conditions imposed upon it during its use, the correction for the cool column projecting into the air may be omitted. This correction, by the way, may account for the fact that Meyerhoffer and Saunders found the transition temperature of sodic sulphate to be only 32·35°* instead of 32·38°.

We are much pleased that the idea should have been grasped with such eagerness in the laboratory of Professor van 't Hoff, for no better proof could be found of its unquestionable utility. We feel too that constants of this sort, like atomic weights, should be studied by more than one set of investigators, and that they should be finally investigated with the utmost care in the Bureau Internationale des Poids et des Mesures, and the Reichsanstalt; hence we are glad to accord to Messrs. Meyerhoffer and Saunders the right which they demand to investigate quintuple points involving sodic sulphate or sodic carbonate. At the same time, we feel that our undoubted priority (our preliminary paper having been finished early in June) allows us to study any desired portion of this field; and for the present, feeling that the simpler systems are the better ones, we shall investigate primarily the salts named above.

Synthesis of Hydroxylamine.—A. Jouve.—Hydrogen and nitric oxide in presence of platinum react in the well-known manner, $NO+5H=NH_3+H_2O$. The author has observed that under certain conditions the reaction may be $NO+3H=NH_2—OH$. The product of the reaction is received into dilute hydrochloric acid, from which the salt of hydroxylamine is obtained. Excess of hydrogen decomposes the hydroxylamine, which is therefore an intermediate product in the reduction of nitric oxide to ammonia.—*Comptes Rendus*, cxxviii., No. 7.

* By a clerical error, Rimbach's table for this correction was stated in our last paper to be on page 143 of Landolt and Börnstein's tables (1894). It is really on page 95.

AN ACOUSTICAL METHOD FOR THE DETERMINATION OF THE MELTING-POINT OF FATS AND WAXES.

By EDWIN DOWZARD, F.C.S.

NUMEROUS methods have been proposed for the determination of the melting-point of fats and waxes. In some the melting-point is the temperature at which the fat undergoes a certain degree of softening, either sufficient to allow a plug of the sample contained in a cylindrical tube to be forced up by the pressure of water, or to allow the sample to form a globule.

When a capillary tube is used there is some uncertainty as to whether the melting-point is that temperature at which the fat commences to liquefy, or that at which it becomes clear and transparent.

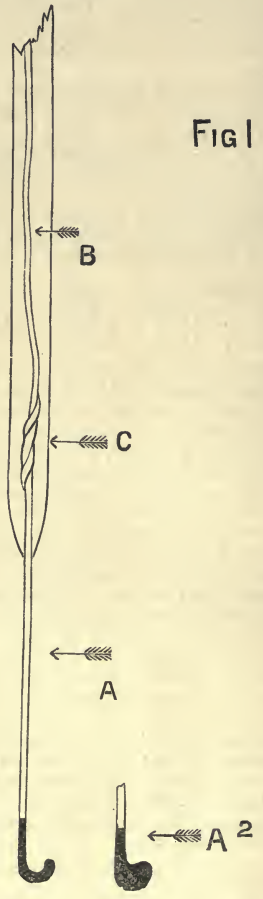


FIG I

On the Continent Pohl's method is frequently used. The bulb of a thermometer is immersed in the melted sample, and quickly removed, so that a thin coating only of fat adheres to it. After several hours the thermometer is inserted into a test-tube so that the bulb is at a distance of half an inch from the bottom; heat is then gradually applied, and the temperature noted at which a drop of liquid fat is observed to form at the bottom of the bulb.

In nearly all the methods that have been proposed there is the method of personal equation.

The method about to be described, which eliminates the error due to personal observation, is based on the following:—Two platinum wires, connected to a battery

FIG 2

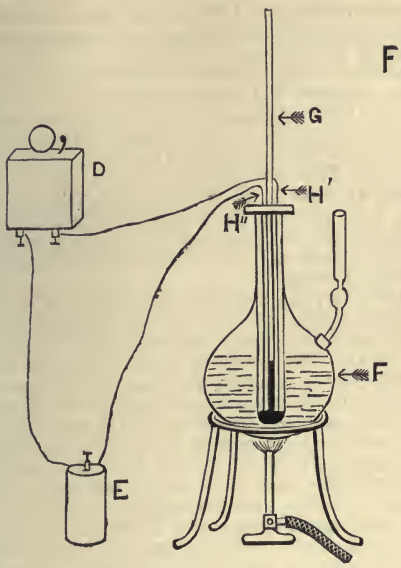
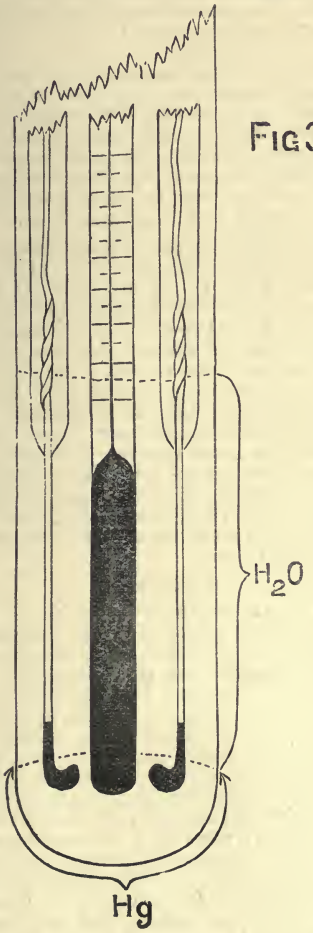


FIG 3



and electric bell, are coated with the fat or wax, and immersed in mercury, which is gradually heated; when the fat melts, the circuit is closed, which is indicated by the ringing of the bell.

Fig. 1, which represents the actual size of the original, consists of a piece of stout platinum wire (A) with a crook at the extremity, fastened to a long piece of copper wire (B); the platinum wire is fused into the glass tube (C), which is about 10 inches long. In the apparatus about to be described there are two of these wires identical in size and shape. The *modus operandi* is as follows;—The sample of fat or wax is melted in a small capsule, the platinum wires are dipped into the melted sample, taken out, allowed to cool, and the process repeated about three times; the wires will then have the appearance of A^2, Fig. 1. The coated wires are allowed to stand for three or four hours, and then placed in the inner tube of a Anschutz and Schulze melting-point apparatus, Fig. 2 (F), along with a thermometer. A quantity of mercury is now introduced into the inner tube, sufficient to allow the wires to be immersed to the top of the crook; water is then poured in until the bulb of the thermometer is completely covered. The outer flask is filled with water to the same level as the water in the inner tube. The wires are now connected with the battery and bell, and the temperature gradually raised; when within about 4 degrees of the probable melting-point the temperature should rise at the rate of about 1 degree in 70 seconds. The reading is taken immediately the bell rings.

Fig. 2 represents the complete apparatus. H' H'' are the wires, and G the thermometer.

Fig. 3 represents the bottom portion of the inner tube (full size).

Of course I do not claim this method to be original, as several chemists have proposed and described various modifications in the way of apparatus.

The above is simply the description of a modified form of apparatus which I have found to give useful and constant results.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 16th, 1899.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. E. Szarvasy, E. B. Fairweather, and Arnold Stevenson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Belton, 103, Lower Seedley Road, Pendleton, Manchester; Robert D. Connell, 38, Chapel Road, Stamford Hill, N.; Harold Francis Carl Goltz, 7, Craster Road, Upper Tulse Hill, S.W.; Robert William Lindsey, 22, Hilldrop Crescent, Camden Road, N.; James MacLeod, Westhill, Cardcross Road, Dumbarton; Allan Frederick Walden, New College, Oxford.

The President announced that he desired to present to the Society a daguerreotype of Dalton, which was one of two taken in 1842. The daguerreotype came into the possession of Mr. Dancer, a philosophical instrument maker of Manchester, who, it might be interesting to state, constructed Joule's thermometers and apparatus, and it was from Mr. Dancer's relatives that he had acquired the portrait. He felt that so interesting a memorial of such a man ought not to remain in the possession of a private individual, and it seemed fitting that its custody should be entrusted to the Chemical Society; he therefore presented it to the Society on the understanding that steps should be taken to ensure its safe preservation.

Through the kindness of Mr. S. W. Woolley, he had received an interesting card which appeared to have been used by Dalton during the meeting of the British Association at Manchester in 1842. This card bears his auto-

graph and an embossed head. Accompanying it was an engraved sheet of symbols representing atomic combinations, which had been prepared to illustrate a paper read by Dalton at this meeting. These he also desired to present to the Society, to be included in the collection of memorials of illustrious chemists which was being gradually formed.

On behalf of the meeting, Professor Tilden thanked the President for the gift of the daguerreotype, which would be preserved with all the care and solicitude which such an interesting memorial deserved. He added that he believed the well-known portrait of Dalton engraved by Jeans, and appearing as the frontispiece in Roscoe and Schorlemmer's "Treatise on Chemistry," was prepared from a drawing made from this daguerreotype.

Of the following papers those marked * were read:—

*42. "*The Boiling-point of Liquid Hydrogen as determined by a Rhodium-platinum Resistance Thermometer.*" By James Dewar, LL.D, F.R.S. (See p. 133).

*43. "*Influence of Substitution on Specific Rotation in the Bornylamine Series.*" By M. O. Forster, Ph.D., B.Sc.

Certain alkyl derivatives of bornylamine have been prepared, in order to ascertain the effect produced by substitution on the specific rotatory power of the base. The following observations have been made:—

1. The specific rotation of bornylamine is largely increased by the replacement of a single hydrogen atom in the amino-group by an alkyl radicle.

2. In ascending the homologous series of monalkyl derivatives, a maximum specific rotation occurs at the ethylic term; if the molecular rotation is considered, the maximum appears at the propylic term.

3. A maximum specific and molecular rotation, occurring at the ethylic term, is also met with in the two series comprising the hydriodides and the benzoyl derivatives of the homologous bases.

4. The specific rotation of bornylamine is slightly increased on replacing both hydrogen atoms in the amino-group by alkyl radicles, but the magnitude of this increase is inconsiderable when compared with that produced by substituting an alkyl radicle for a single atom of hydrogen.

5. The specific rotatory power of paranitrobenzylbornylamine approximates more closely to that of benzylbornylamine than does that of the orthonitro-compound, but this does not apply to the molecular rotation.

6. When an alkyl group replaces hydrogen of the ammonium radicle in the series of alkylbornylammonium iodides, the specific rotatory power of bornylamine hydriodide, instead of undergoing increase in the positive direction, becomes reduced to feeble lævorotation.

7. The monalkylbornylamines, although strongly dextrorotatory, give rise to benzoyl derivatives which are strongly lævorotatory.

The following bases have been prepared and examined. *Methylbornylamine*, *dimethylbornylamine*, *ethylbornylamine*, *diethylbornylamine*, *normalpropylbornylamine*, *isopropylbornylamine*, *butylbornylamine*, *benzylbornylamine*, *orthonitrobenzylbornylamine*, and *paranitrobenzylbornylamine*. Certain salts of these compounds have been also characterised.

Discussion.

Dr. Armstrong said that mere simple relations of mass were by no means the sole controlling influences in the case of other properties, and it would be surprising had optical activity been found to be an exception to the rule. In all experiments on optically active compounds it was difficult to discount the effect of association which, as other workers in the field had suggested, might afford an explanation of divergencies in a series of homologues such as those recorded by the author. The marked differences in the rotatory powers of the alkyl- as compared with the dialkyl-bornylamines, was only an additional illustration of the fact that asymmetry has an influence entirely different from that of symmetry on the properties of substances.

Dr. Lewkowitsch suggested that interesting results would be obtained if the author were able to prepare a homologue of dimethylbornylamine methiodide in which the two methyl groups were replaced by two different alkyl groups of greater mass, say, by propyl and butyl respectively. The nitrogen would thus become asymmetric, and as, from Le Bel's experiments (*Compt. Rend.*, 1890, cx., 144), it might be expected that optical activity would ensue, the examination of a product containing asymmetric carbon and nitrogen atoms could not fail to give important results.

Dr. Crossley remarked that the curious behaviour of the isopropyl group, referred to by the author, was not at all uncommon in the case of ethereal salts of substituted malonic acids. For example, α-ethyl- and αα'-methylethyl-pimelic acids could be prepared by the interaction of the ethereal salts of corresponding substituted malonic acids with trimethylene chlorobromide (*Trans.*, 1894, lxv., 987), but similar experiments made with the object of preparing methylisopropylpimelic acid had not given satisfactory results, and up to the present had not been completed. Another example was to be found in the preparation of ethylisopropylacetic acid from the corresponding malonate, the introduction of the isopropyl group being attended with great difficulty. It would be of interest to know what was the effect on the rotatory power of substituting dissimilar alkyl radicles in bornylamine.

Dr. Forster, in reply, stated that practical difficulties had hitherto prevented the examination of the derivatives of bornylamine to which Drs. Lewkowitsch and Crossley had referred. It had not been possible to prepare by direct methods either unsymmetrical alkylbornylammonium iodides or dialkylbornylamines, but this object had been kept in view, and an attempt would be made to deal with the question at some future time.

*44. "*Contribution to the Characterisation of Racemic Compounds.*" By A. Ladenburg, For. Mem. C.S.

The author refers to the fact that his definition of racemism has not received confirmation from the experiments of Kipping and Pope, but believes that the principle involved in it is correct, and has only been expressed in a misleading manner. He therefore substitutes the following:—To characterise an inactive substance, determine its solubility with and without the addition of one or other of its optically active components at the same temperature and with the same solvent. If the solubilities are different, the substance is a racemic compound; if the same, it is an enantiomorphous mixture. Experiments with racemic acid, *i*-pyrotartaric acid, and an inactive mixture of sodium ammonium *d*- and *l*-tartrates, are given in support of this view.

Discussion.

Mr. W. J. Pope said he was gratified to learn that Professor Ladenburg agreed with the criticism passed by Kipping and himself (*Trans.*, 1899, lxxv., 36). upon the older work respecting the characterisation of racemic compounds. The amended form into which Professor Ladenburg cast his statement was not, however, identical in principle with the older one, as the two statements involved absolutely different principles. The older statement said that the solution of a non-racemic optically active mixture of antipodes should deposit, on crystallisation, a mixture of the antipodes of the same composition as that in solution: this view Kipping and he had shown to be untenable. Professor Ladenburg's new statement was quite independent of any similarity of composition between the mixture in the solution and that in contact with the solution; it merely embodied the principle which Kipping and he had stated, and shown to be true by experiments on mixtures of sodium ammonium dextro- and lævo-tartrates, namely, that the most soluble non-racemic

mixture of two enantiomorphously related substances is a mixture in equal proportions. The facts (*a*) that a racemic compound had a different solubility alone than when mixed with one of its enantiomorphous constituents, and (*b*) that an inactive non-racemic mixture of two antipodes had the same solubility as a mixture containing excess of one constituent, were simple consequences of the phase rule. In case (*a*), the solution in equilibrium with the racemic compound was saturated with respect to a single substance only, but on adding one of the active components the solution became either saturated with respect to two substances—the racemic and the active—or saturated with regard to the racemic substance and partially saturated with respect to the active substance; in either case, as Professor Ladenburg found with the tartaric and pyrotartaric acids, the solution changed in concentration. In case (*b*), the solution in equilibrium with, and in contact with, the non racemic inactive mixture was saturated with respect to both *d*- and *l*-constituents, and addition of excess of one solid constituent did not affect the mixture going into solution, because it did not alter the solid phases in contact with the solution. Thus Professor Ladenburg found the solubility of a compensated mixture of sodium ammonium *d*- and *l*-tartrate to be the same as that of non-compensated mixtures; from the work of Kipping and himself it was to be premised, not only that the solutions were in both cases equally concentrated, but were both inactive, containing equal quantities of the *d*- and *l*-isomerides. He could not agree with the view that Professor Ladenburg's experiments proved that "ammonium sodium *d*- and *l*-tartrate remain uncombined in the solution"; the experiments proved merely that the *d*- and *l*-salt in contact with the solution were uncombined, but threw no light on the condition of the dissolved material. Professor Ladenburg's new statement was indisputable; it was corroborated by the work of Kipping and himself, and had nothing in common with his older definition of racemism.

Dr. Lewkowitsch suggested that the examination of a racemic compound which was more soluble in water than its optical isomerides would complement in some way the results obtained with racemic acid, which was less soluble than either dextro- or lævo-tartaric acid.

45. "*Rotatory Powers of Optically Active Methoxy- and Ethoxy-propionic Acids prepared from Active Lactic Acid.*" By Thomas Purdie, F.R.S., and James C. Irvine, B.Sc.

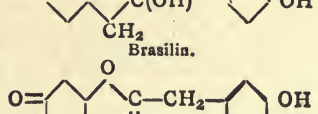
The authors have applied the method of alkylating the ethereal salts of hydroxy-acids by means of alkyl iodides and silver oxide (*Trans.*, 1899, lxxv., 157) to lævo-rotatory methylic and ethylic lactates, and have obtained methylic methoxypropionate and ethylic ethoxypropionate, the specific rotations of which at 20° were found to be $-95{\cdot}53°$ and $-79{\cdot}69°$ respectively. These high values, and the fact that the rotations are of the same sign as that of the lactates, confirm the conclusion that the alkyl lactates made from the silver salt owe their high activity to the presence of small quantities of alkyloxypropionates.

Anhydrous methoxy- and ethoxy-propionic acids, as well as ethylic methoxy- and methylic ethoxy-propionates, were prepared; the molecular rotations of the anhydrous acids were about equal to one another, and those of the methoxypropionates higher than those of the corresponding ethoxy-compounds, a result which seemed to be at variance with previous observations (*Trans.*, 1898, lxxiii., 862) on the metallic salts of the same acids otherwise obtained, according to which the methoxypropionates were the less active. The molecular rotations of the metallic salts of the two acids obtained as above, however, confirm the previous observations. Curves representing the decrease of rotation with increasing concentration show that the factor causing the decrease has a greater effect on the methoxy- than on the ethoxy-salts, and that the difference is more marked in the case of the salts of divalent metals.

The rotations of the acids in aqueous solutions are less than in the anhydrous state, and are nearly constant on dilution, that of the methoxy-acid, as in the case of the ethereal salts, being the higher. It seems probable that the anhydrous acids contain molecular aggregates of higher activity than the individual molecules or ions, and that the higher activity of the methoxy-acid in aqueous solution, as compared with the ethoxy-acid, is due to the acid, like the salts, being more influenced by this factor.

46. "*On Brasilin and Hæmatoxylin.*" II. By A. W. Gilbody and W. H. Perkin, jun.

In continuing their investigations on the constitution of these substances, the authors oxidised dimethylbrasilin with permanganate, and obtained in this way an acid melting at 173°, which, on analysis, gave numbers agreeing with those required for the formula $C_{10}H_{10}O_6$. This acid is dibasic, the silver salt having the formula $C_{10}H_8Ag_2O_6$; it is characterised by great stability, permanganate only attacking it with difficulty at 100°; it gives no coloration with ferric chloride, but when fused with potash, and the acidified product extracted with ether, a substance is obtained which gives with ferric chloride an intense violet coloration, and is, therefore, probably resorcinol, or one of its derivatives. After a careful study of the various new oxidation products described in their previous communication (*Proc.*, 1899, p. 27), the authors conclude that brasilin and brasilein are probably represented by the formulæ—

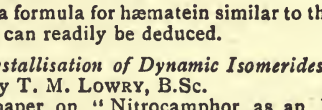


Brasilin.

Brasilein.

but they must reserve for the detailed paper the reasons which have led them to this conclusion.

If the formula for brasilin should prove to be correct, the constitution of hæmatoxylin will probably be represented by the formula—



from which a formula for hæmatein similar to that assigned to brasilein can readily be deduced.

47. "*Crystallisation of Dynamic Isomerides.*" A Correction. By T. M. Lowry, B.Sc.

In his paper on "Nitrocamphor as an Example of Dynamic Isomerism," the author states (*Trans.*, 1899, lxxv., 231) that the laws governing the crystallisation of isodynamic substances had not yet been discussed, and the behaviour of nitrocamphor and π-bromonitrocamphor on crystallisation is used as a basis for the theoretical treatment of the subject. A paper by Roozeboom, entitled "Ueber die Erstarrung flüssiger Mischungen tautomerer Stoffe," which has just appeared (*Zeit. Phys. Chem.*, 1899, xxviii., 289) has drawn the author's attention to the fact that he had unfortunately overlooked the full theoretical discussion of the subject by Bancroft in two papers on "The Equilibria of Stereoisomers" (*Journ. Physical Chem.*, 1898, ii., 143, 245). The behaviour of nitrocamphor and π-bromonitrocamphor, and the conclusions arrived at from the study of these two special cases, are completely in accord with the general laws deduced by Bancroft.

PHYSICAL SOCIETY.

Ordinary Meeting, March 24th, 1899.

Prof. OLIVER LODGE, F.R.S., President, in the Chair.

Mr. W. R. COOPER read a paper by Mr. A. P. TROTTER on "*The Minor Variations of the Clark Cell.*"

The author describes a series of experiments in which he compared the E.M.F.'s of certain standard cells at frequent intervals from July, 1896, to February, 1897, at Cape Town, where the temperature of the double box containing the cells varied between the limits 13° C. and 28° C. One cell was selected for comparison with all the others. No special precautions seem to have been taken to keep the temperature of this selected cell constant. The observed differences between the E.M.F.'s of the respective cells rarely exceeded 0·001, corresponding to about a quarter of an inch on the slide-wire of the potentiometer. Details as to the area of the slider-contact are not stated; the readings are generally taken to the fourth decimal, *i.e.*, to one-tenth of a millivolt, and occasionally to one-fourth of this. Temperature was read to 0·1° C. on a mercury thermometer placed through a hole in the double box containing the cells—not in the cells themselves.

Mr. E. H. GRIFFITHS said that the paper appeared to have value only in so far as it showed that Clark cells at Cape Town behaved in a manner that agreed with common knowledge and general experience everywhere else. Their variations depended upon shifts of temperature, and the consequent changes in the degree of saturation of the liquid. From his own experiments during seven years, upon 42 Clark cells, he had shown that if temperature was kept constant to within 0·01° C., the steadiness and uniformity of all the E.M.F.'s was most remarkable. They started with discrepancies, but at the end of the time it was impossible to detect any differences. It was of little use to put a thermometer anywhere but within the cells; very slight changes of temperature caused serious changes in the degree of saturation of the liquid. The existence of the capricious lag of E.M.F. behind temperature precluded the possibility of formulating a temperature correction for Clark cells. In the case of Callendar cells there was no lag; their E.M.F. varied slightly with temperature, by a definite amount, which could be corrected by a coefficient.

Mr. W. R. COOPER said the method of comparison used by the author was unsuitable because to arrive at the differences of E.M.F., necessitated the measurement of the E.M.F. of each cell. The variations only amounted to a few ten-thousandths of a volt. The length of potentiometer-wire corresponding to a thousandth of a volt was only a quarter of an inch; under such conditions it would be difficult to ensure accuracy. A method of opposition would have been preferable. Mr. Cooper had found that Board of Trade cells only vary about one ten-thousandth of a volt between themselves from day to day. Cells of the H form vary about one-fifth of that amount.

Prof. J. D. EVERETT then read a paper by Dr. E. H. BARTON and Mr. W. B. MORTON on "*The Criterion for the Oscillatory Discharge of a Condenser.*"

The object of the paper is to inquire how the condition for the oscillatory discharge of a condenser is modified when the ordinary differential equation of the second degree is supplemented by the terms added by Maxwell to take account of the distribution of current in the (straight) wire. The coefficients of these terms are relatively small, so that the algebraic equation giving the periods is a quadratic with small terms of higher order added. The effect of these higher terms is, first, to introduce very rapid vibrations of small amplitude; and next, to displace the roots of the unaltered quadratic. The nature of the discharge—oscillatory or non-oscillatory—may be taken to be determined by these principal roots, and the critical case is when they are equal. The condition for equality is obtained, by the property of the derived function, as a series of powers of the small coefficients of the equation, which may be carried by successive approximation as far as is desired. The paper also treats the question by an alternative and more physical method, which consists in replacing the resistance, inductance, and capacity that occur in the ordinary formula, by modified values. This gives the criterion correct to the third order in the small terms. It is shown that a condenser satisfying the critical condition on the simple formula would, when the added terms are taken into account, give an oscillatory discharge.

Prof. LODGE said that the result naturally to be expected of "throttling," viz., the increase of resistance, and decrease of self induction, due to the current keeping to the outside of the conductor, would tend rather to damp out the oscillations than to favour them.

Prof. EVERETT observed that the equation was no longer a quadratic, and that the quadratic criterion as to whether the discharge was oscillatory or non-oscillatory did not hold. The paper appeared to be consistent with itself, and he considered that ths authors had satisfactorily proved, in their discussion of the equation of current, that the effect of "throttling" was to increase the tendency towards the oscillatory mode of discharge.

Prof. LODGE admitted that the quadratic criterion did not hold; he thought it most likely that the authors, who evidently had gone into the matter with care, were right. At the same time he wished to call attention to the singular and unexpected character of their conclusion. If it turned out that it was correct, *i.e.*, that there was no slip in sign, it was a result upon which he would desire to congratulate them.

The PRESIDENT proposed votes of thanks, and the meeting adjourned until April 21st.

CORRESPONDENCE.

ANALYSIS OF THE ASH OF CARDAMOMS.

To the Editor of the Chemical News.

SIR,—In CHEMICAL NEWS (vol. lxxix., p. 122) appears a quantitative estimation of the ash of the cardamom fruit by Mr. H. B. Yardley, and, to my surprise, no mention is made of the presence of manganese, which, I believe, is always present—although in small proportions—in the ash of genuine cardamoms.

In order to satisfy my curiosity upon the point, I have referred to several standard works upon Materia Medica, and I find most of them give manganese as one of the ash constituents. Thus, in Maisch's "Materia Medica" it is stated that "Ceylon cardamoms yield 15 per cent of ash, containing 0·8 per cent of manganese;" Flückiger and Hanbury's "Pharmacographia" mentions "the ash is remarkably rich in manganese;" whilst in the "Year-Book of Pharmacy" for 1898 occurs, "Shaer states that the presence of manganese in the ash of genuine cardamoms, and its absence in other species of *Amomum*, serves as a distinction."

It would be interesting to know whether Mr. Yardley confirmed these statements or not.—I am, &c.,

HERBERT BRIDGES, Ph.C.

74, Park Lane, Norwich,
March 18, 1899.

THE ESTIMATION OF POTASH.

To the Editor of the Chemical News.

SIR,—Referring to the article on "The Estimation of Potash" in the last number of the CHEMICAL NEWS (vol. lxxix., p. 135), I beg to make the following remarks:—

The described way of estimation has been used for

years in the Official Versuchsstationen of Germany, and answers very well. There is one difference: instead of adding barium carbonate to the alkaline solution, the barium hydroxide is added at first to the acid solution (hydrochloric acid) and then ammonium carbonate, which changes the free barium oxide or the barium chloride into barium carbonate, whilst it does not act on the barium sulphate formed. This way is preferable, since the double decomposition between sulphates and the barium carbonate is not perfect in alkaline solution.—I am, &c.,

WILLY JERWITZ, Ph.D.

The Glen, Cork.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

SIR,—Recently I had occasion to make a test of a sample of caustic soda for available soda. As the sample had been imported from England, an English test on the 32 equivalent was asked for.

Not having a special acid solution on hand, I concluded the simplest method would be to calculate from the 31 equivalent value. The following is my method of calculation:—

The molecule of NaHO on the 31 equivalent is 40, and contains 31 parts Na_2O, which is equal to 77·5 per cent. On the 32 equivalent, NaHO equals 41 and contains 32 parts of Na_2O, which is equal to 78·05 per cent; a difference of only 0·55 per cent between the two equivalents.

On referring to the tables in Lunge's "Treatise on Alkali Manufacture" (vol. ii., p. 109), I found the difference ought to be 1·02 per cent. It would appear Lunge calculates his results from the relative percentage of Na_2O in Na_2CO_3 on the 31 and 32 equivalents. This proceeding is obviously wrong for caustic soda. It seems an extraordinary thing that such an error should have been made and remained undetected by Prof. Lunge.

Of course, one may say that a difference of 0·4 to 0·5 per cent on the available soda in a caustic soda test would not make much difference. But when it is considered that on a high strength caustic soda everything over, say, 76·5 per cent, is reported as 77 per cent, and everything under the same 76 per cent, a difference of 0·4 per cent would be very often as bad to the manufacturer as 1 per cent.

Is it not time for caustic soda consumers to combine and insist on the complete abolition of the 32 equivalent?—I am, &c.,

H. A. HOOPER.

Chicago, Ill., U.S.A.

ERYTHROL TETRANITRATE.

To the Editor of the Chemical News.

SIR,—An accident, by which a chemist lost his life, happened at a tabloid factory at Dartford, on the 15th of December, 1897. He was engaged in mixing tetranitrate of erythrol, with finely powdered lactose in a mortar, when an explosion occurred.

Again, at the end of 1898, an accident was caused by tetranitrate of erythrol being inadvertently thrown into a fire, and one person was injured.

Tetranitrate of erythrol is possessed of explosive properties, and is highly sensitive, more so indeed to percussion than dynamite or gun-cotton. As it has lately come into some use, in the place of nitro glycerine, as a remedy for angina pectoris, I should be glad if you would draw special attention in your paper to the dangers attending the handling of this drug.—I am, &c.,

A. FORD, Colonel,
H.M. Chief Inspector of Explosives.

Home Office, Whitehall, S.W.,
March 24, 1899.

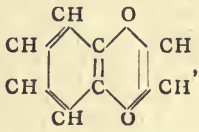
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

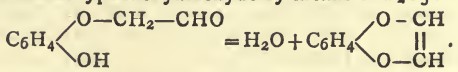
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 9, February 27, 1899.

Phosphorescence of Strontium Sulphide.—J. R. Mourelo.—The author has obtained, by the modified method of Verneuil, sulphides of strontium, calcium, barium, and zinc which present a greater and more persistent phosphorescence after exposure to diffused daylight than to the direct rays of the sun for the same period of exposure. In fact, the yellowish green luminosity characteristic of strontium sulphide is never properly obtained from specimens which have been exposed in direct sunlight. The reason is probably that the light waves of greatest amplitude exert the greatest influence, the exciting force in this case being in the invisible portion of the radiation. Radiation from the nearly colourless "Bunsen" flame and from iron heated to a temperature lower than that of redness, is sufficient to produce phosphorescence. One portion of strontium sulphide whilst phosphorescing can excite phosphorescence in another in its neighbourhood.

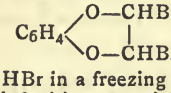
Ethylene Pyrocatechin.—Ch. Moureu.—Ethylene pyrocatechin,—



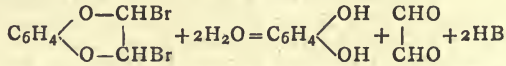
is the first body known which contains a dioxybenzene nucleus combined with an unsaturated radicle. It is obtained in very small amount by the action of acetyl chloride either on orthoxy-phenoxyacetal or on ethoxy-ethane-pyrocatechin; these methods are only of theoretical importance. In practice, it is easily obtained by dehydration of orthoxyphenoxyaldehyde by means of P_2O_5:—



Ethylene pyrocatechin is a colourless oil boiling at 193°. It readily gives the dibromide,—



when treated with HBr in a freezing mixture. This body saponifies when boiled with water, giving glyoxal and pyrocatechin, according to the following equation:—



Method of Estimating a Composition of the Oils of Acetone.—A. and P. Buisine.—The authors have devised a means of determining, as simply as possible, the composition of the oils of acetone obtained from the liquors of wool manufactories. The separation of the products, which constitute oil of acetone, is long and laborious, but it is a sufficient test of the composition to determine the density, solubility in water, solubility in acid sodium sulphite, and the volume of the liquid which distils over between known limits of temperature. The method of procedure for those determinations is indicated.

Combinations of Phenylhydrazine with Alcoholic Iodides.—P. Genvresse and P. Bourest.—There is a violent reaction between ethyl iodide and phenylhydrazine even at low temperatures, unless the two bodies are in solution. The authors experimented with solutions of ethyl and methyl iodides respectively, and these gave with phenylhydrazine well crystallised products. Two

products were obtained in each case; one soluble, the other insoluble in absolute alcohol. The insoluble compound had the formula $C_6H_5NH.NH.R_2I$; and the soluble compound, $(C_6H_5NH.NH_2)_2RI$.

No. 10, March 6, 1899.

Bisulphide of Tungsten.—Ed. Defacqz.—Riche's method of preparing the bisulphide of tungsten consisted in heating a mixture of equal weights of sulphur and potassium bitungstate, previously prepared by fusing the neutral tungstate and tungstic acid in the ratio of their molecular weights. The author has modified this method and devised a second. 1. *Action of Hydrogen Sulphide on Tungsten Hexachloride.*—The hexachloride is placed in a boat inside a glass tube, which is drawn out into two bulbs at one end. After completely removing the air with a current of H_2S, the tube is gently heated. The reaction begins at 375°, and the temperature is raised to 550° for some time; the bulbs are then removed and the sulphide collected. 2. *Modification of Riche's Method.*—An intimate mixture of pure dry potassium carbonate, flowers of sulphur, and the oxide WO_3 is made in the following proportions:—138 parts K_2CO_3, 464 parts WO_3, 558 parts S. The whole is put in an earthen crucible and heated in an oven, first to dull redness, then—when the reaction is over—to the fusion-point. After allowing to cool, the crucible is broken, the black mass coarsely powdered, washed with (1) cold water, (2) hot water, and finally filtered. The bisulphide obtained by the first method oxidises readily by means of aqua regia to tungstic and sulphuric acids; the other oxidises with less readiness. For analysis, the body is fused in a platinum crucible with a mixture of KNO_3 and K_2CO_3; the cooled mass is dissolved in water, acidulated with HCl, and evaporated to dryness. The residue is extracted with water; insoluble tungstic acid remains behind, and the sulphur in the solution is estimated as barium sulphate. The metal is estimated as WO_3. Prepared from H_2S and WCl_6, the bisulphide consists of amorphous black scales; prepared by the second method, it is in the form of small crystals. Heated in the air, it burns; but undergoes change of composition when heated to exceedingly high temperatures away from air. Towards 400°, chlorine readily converts it into the hexachloride.

Action of Formic Aldehyde on Menthol and Borneol.—A. Brochet.—Formaldehyde reacts with alcohols to give formals of the general formula $CH_2(OR)_2$. The author has obtained dimentholic formal, $CH_2(OC_{10}H_{19})_2$, and diborneolic formal, $CH_2(OC_{10}H_{17})_2$.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements after Easter at the Royal Institution:—Professor J. Cossar Ewart, three lectures on "Zebras and Zebra Hybrids"; Professor Silvanus P. Thompson, two lectures on "Electric Eddy-currents" (the Tyndall Lectures); Professor W. J. Sollas, three lectures on "Geology"; Professor Dewar, three lectures on the "Atmosphere"; Mr. Lewis F. Day, three lectures on "Embroidery"; Professor L. C. Miall, two lectures on "Water Weeds"; Mr. Louis Dyer, three lectures on "Machiavelli"; Mr. W. L. Brown, two lectures on "To Iceland in Search of Health"; Mr. Edgar F. Jacques, three lectures on the "Music of India and the East, and its Influence on the Music of Europe" (with musical illustrations). The Friday Evening Meetings will be resumed on April 14th, when a discourse will be delivered by Professor A. W. Rücker on "Earth Currents and Electric Traction." Succeeding discourses will probably be given by Dr. F. W. Mott, Professor C. A. Carus Wilson, Dr. W. J. Russell, Professor T. Preston, The Right Rev. the Lord Bishop of Bristol, Sir William Martin Conway, Mr. H. G. Wells, and other gentlemen.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2054.

ON THE REDUCTION OF CHROMIC ACID BY ACETIC ACID, AND ITS EFFECT IN ANTHRACENE TESTING.

By HENRY BASSETT.

In the course of a series of experimental anthracene tests, lately carried out, some decided irregularities in the results were observed, for which it was very difficult to account. Eventually, however, they were found to arise from the acetic acid employed, and the result of the enquiry is, I believe, of sufficient importance to be put in evidence.

The acetic acid in question was of presumably good quality, and crystallised at 56° F.

I had long ago noticed that the usual chromic solution, which when freshly prepared is of a clear red colour, soon became browner and less transparent, indicating slight reduction; I therefore made comparative experiments with the acid referred to, and with the best acid crystallising at 62° F., and found very marked differences between them.

Two solutions were prepared exactly as used in the ordinary test (with chromic acid of 98 per cent), one with the acetic acid crystallising at 56°, the other with pure acid crystallising at 62°.

These solutions were analysed at intervals of a few days, and the reduction gradually increased in both cases, but much more slowly with the pure acid. After 24 days it represented a loss of 0·16 grm. chromic acid with the pure acetic acid, and to no less than 0·87 grm. chromic acid when using the inferior acetic acid, out of the 15 grms. used for a test.

These results indicated the presence of small quantities of aldehyde, acetone, &c., in the inferior acid, which was confirmed by its behaviour with silver salts.

It then became necessary to find out what reduction took place in a boiling solution. Experiments were made with the pure and inferior acetic acids precisely as in ordinary anthracene testing; *i.e.*, with exactly the same proportions of chromic acid, acetic acid, and water, but *minus* the anthracene. After four hours' boiling the reduction was found to correspond to 4·44 grms. chromic acid with the pure acetic acid, and to 6·45 grms. with the inferior acid (calculated as before on to the 15 grms. used for a test).

These unexpected results led me to try the effect of more or less water; in a few words, with equal volumes of acid and water the reduction became almost *nil*, but, on the other hand, by using pure acetic acid without any water, after boiling for about ten hours the solution on cooling became a mass of crystals of chromic acetate, and the reduction was found to have extended to more than two-thirds of the total quantity! The same formation of crystals, &c., was obtained with the usual proportion of water, but only after boiling for, say, 48 hours.

The generally accepted statements in text-books, that acetic acid is scarcely attacked by chromic acid, are completely contradicted by these results, and it is almost unnecesary for me to point out their bearing on anthracene testing. In the first place, when using an inferior acetic acid, higher results will be obtained from the greater destruction of chromic acid during the boiling. This difference, from my experiments with the acid referred to above, amounts to (say) 0·4 per cent of anthracene.

Secondly, with inferior acetic acid the oxidising mixture will lose strength by keeping for some time. This is probably the cause of many unexplained discrepancies, as for convenience this mixture has commonly been prepared in some considerable quantity, and it is obvious that tests made with the last portions of the stock (which may have been kept a long time) will be higher than subsequent tests made with a freshly prepared mixture. My actual experimental results have given a difference of, say, 0·3 per cent of anthracene when using a mixture a month old.

Comparative experiments with pure acetic acid and freshly prepared oxidising mixture, against inferior acid and old mixture, gave confirmatory results, the difference being approximately the sum of the two above mentioned.

These results show the reason why the very large quantity of 15 grms. chromic acid should have been found necessary to oxidise 1 grm. of anthracene, much more being used up by the acetic acid than by the anthracene itself. I may add here that I have proved by analysis of filtrates from the crude quinones that half the chromic acid (say 7·5 grms.) remains unreduced.

Finally, the indications are that only pure acetic acid crystallising at, say, 62° F. should be used, and that the oxidising mixture should not be more than 15 days old.

104, Queen Victoria Street, E.C.

MISCELLANEOUS NOTES.

Opening up Specular Iron Ores.

The specular variety of hæmatite, such as is mined in Elba, for instance, contains crystals of ferric oxide which, though easily crushed to small laminæ, are not easily ground, even in an agate mortar, so finely as to be quite soluble in acids. The glistening of the small plates is apparent when a moderate amount of patience has been exhausted in grinding enough of the ore for a complete analysis.

A preliminary fusion does not always overcome the difficulty, and it is objectionable in that it introduces a considerable amount of fixed alkaline salts; a point of some moment where great care is being taken to avoid the accumulation of such compounds in passing from the estimation of silica to the estimation of magnesia on the same sample. It cannot come amiss, then, to describe an alternative procedure which neither needs laborious grinding of the sample nor introduces material amounts of impurity.

The ore, which is sufficiently fine after passing through a sieve of 90 meshes to the lineal inch, is boiled with hydrochloric acid and diluted with some clippings of soft ashless paper which have been beaten to a pulp in water. With constant agitation this mixture is poured on to a pulp filter and washed. The pulp, which is now uniformly grey, owing to the thorough dissemination of the small crystals, is transferred to a crucible, dried, and then charred at the muffle's mouth. The crystalline ferric oxide is reduced by the glowing mass of carbonised paper as it would be in the blast furnace; but later, when the combustion of the paper is completed and the crucible is more strongly heated, the iron is re-oxidised. The glistening appearance is now gone, and except a little silica the solution is easily completed by boiling with strong hydrochloric acid.

Manganese in Chrome Steels.

Steels containing a few per cent of chromium are rarely perfectly soluble in nitric acid, and, not unfrequently, the solution cannot be completed either by long boiling or by subsequent addition of potassium chlorate. On this account, using Ford and Williams's method of estimating manganese in such steels, the precipitated manganese

oxide is accompanied with more or less of a metallic residue. Besides the possibility of these particles containing manganese they afford a greater though less apparent source of error.

The ferrous ammonium sulphate solution by which the manganese di-oxide is to be volumetrically estimated always contains considerable free acid, must in fact have free acid present in order to complete the subsequent reaction with permanganate or bi-chromate. This free acid attacks the metallic particles, forming either more ferrous sulphate or in other ways reducing that which has been already oxidised.

Perhaps the adoption of an altogether different method is the shortest way out of the difficulty—if it is a frequently recurring one.

CHROMIUM IN FERRO-CHROMIUM.

A similar but still more subtle error may vitiate the estimation of chromium in ferro-chromium when certain processes are used. The general process referred to is the heating of the finely powdered alloy at a high temperature with strongly basic reagents so as to form chromates. The sintered (or maybe fused) mass is placed, crucible and all, into a beaker containing dilute sulphuric acid. Finally the chromic acid is titrated with ferrous sulphate and bichromate.

If any of the powdered alloy were incompletely oxidised its amount would represent not only so much loss, but by dissolving in the dilute acid solution it would reduce some of the already oxidised portion. The subtilty of the danger lies in the fact that amid the general effervescence which accompanies the contact of the acid and the ignited compound, a small error of this kind is not visibly indicated, and the small amounts usually operated upon render an error which is small absolutely of considerable moment when stated in percents.

An obvious precaution is to boil the solution with permanganate, the excess of which is destroyed by dilute hydrochloric acid after the manner of Stead's improved acid permanganate process.

J. T.

A NEW FILTERING MEDIUM.*

By GEO. WM. SARGENT and J. KIRK FAUST.

FOR the removal of manganese dioxide from the nitric acid in which solution it has been precipitated by potassium chlorate, a glass tube similar to that used for carbon determinations is recommended. The bottom of this tube is covered first with a small piece of glass-wool, then with asbestos. This we used for some time, but were frequently troubled by the precipitate runnning through, unless a very thick bed of asbestos was made. In this case the time consumed in filtering was very considerable, due to clogging of the filter by potassium chloride from the large amount of potassium chlorate necessary to oxidise the chromium which was present in considerable quantities in the steels dealt with.

After some experimenting we adopted the following as giving the most satisfactory results:—A carbon filtering-tube with a stem 5 inches long, and a body 3½ inches long and 1¼ inches in diameter, is filled ¼ inch with pewter sand, a small piece of glass-wool being used to retain the sand; over this a thin layer of asbestos is formed by pouring in the asbestos shaken up with water and sucking the bed dry. A little hot dilute nitric acid is poured back and forth through the tube several times, when it is ready for use.

When a heavy precipitate is encountered, the bulb from a syringe is used to force air into the tube and drive the liquid through, care being taken to keep the bulb compressed until removed from the tube.

* Read at the New York Meeting of the American Chemical Society, December 28, 1898.

We have found that the quickest and best way to wash the manganese dioxide consists in allowing the nitric oxide to run entirely through the filter, then washing all the residue in the beaker into the tube with cold water, and, as soon as the filter is drained, washing out the potassium chloride with hot water. The filter and manganese dioxide are blown out into the beaker, and the dioxide reduced with ferrous sulphate, &c. The sand and asbestos are recovered and used time and again. The washings and nitric acid filtrate were examined and found free from manganese. In this filtrate the chromium was determined by adding ice and reducing the chromate with ferrous sulphate, &c.*

This sand filter was used for the removal of ammonium phosphomolybdate from the solution in which it was precipitated. It was found best to place a few pieces of glass rod upon the asbestos to hold it in position when the solution was first being poured upon the filter. With this device we have found the freeing of the precipitate and filter of molybdic acid to be more easily and more quickly accomplished than when paper filters were used. The phosphomolybdate has a tendency, as all know, to creep, and, unless the filter is fitted properly to the funnel, to

get into the filtrate. This trouble is avoided by the sand filter. To dissolve the precipitate, the ammonia solution is poured through the filter two or three times, and finally washed out with hot water. A number of determinations, using the sand and paper filters side by side, have been made on the same sample, and the results obtained agreed to a thousandth. It was found best to wash the sand filters, used to catch the ammonium phosphomolybdate, with ammonia as well as with nitric acid, since in the ammonia washings silica and alumina were found, and these would tend to clog the reductor.

Once made up they stand ready for repeated use, and besides saving time they save considerable money, especially where many determinations are made. By these filters one man was able to turn out in one day forty-two phosphorus determinations, and every precipitate was washed until the droppings from the tube gave no reaction for molybdenum when tested with ammonium sulphide.

* "Methods for the Analysis of Ores, Pig Iron, and Steel," compiled from the *Transactions of the Chemical Section of the Engineers' Society of Western Pennsylvania.*

The cut shows clearly the manner of making up these filters.—*Journal of the American Chemical Society*, xxi., No. 3, March, 1899.

ANALYSIS OF THE WATER OF THE GREAT OR ILLECILLIWAET GLACIER, B.C.

By FRANK T. SHUTT and A. T. CHARRON.

In August last we submitted to analysis two samples of water obtained from the Great or Illecilliwaet Glacier, B.C. These waters, collected on the 7th and 19th of August, respectively, were taken within a few feet of the Glacier's irregular face, about 1½ miles from Glacier Station on the Canadian Pacific Railway. Throughout the summer months numberless streams of ice-cold water flow from the melting face of the Glacier, to form a foaming torrent that rushes down the valley to join the Illecilliwaet River. All who have been through the mountains will remember that the characteristic feature of the Glacier streams is their turbid—or better described as *milky*—appearance, the cause of which we have ascertained to be finely divided rock matter (principally quartzite) in suspension.

The samples, which arrived at our laboratories on August 15th and 24th, were immediately examined, with the following results:—

Chemical Analysis.

	No. 1. Collected Aug. 7. Analysed „ 15.	No. 2. Collected Aug. 19. Analysed „ 24.
	Parts per million.	
Free ammonia	0·018	0·018
Albumenoid ammonia	0·027	0·037
Nitrogen as nitrates and nitrites	0·0246	0·0442
Oxygen absorbed in 15 minutes	0·0396	0·0672
„ „ 4 hours	0·1056	0·1744
Chlorine	0·10	0·10
Total solids at 105° C.	30·8	12·0
Solids after ignition	30·8	8·0
Loss on ignition	None	4·0
Phosphates	None	None.

From the above data we may unhesitatingly conclude that the Glacier water is one of great organic purity. The samples are not identical, due no doubt to the fact that they were collected twelve days apart, and probably from different parts at the foot of the Glacier. Both analyses, however, show that, judged by the standards used in the diagnosis of ordinary potable waters, it is a water possessing a high degree of purity, and one perfectly wholesome and eminently suited for drinking and household purposes.

As received, both samples were quite murky, almost milky, in appearance. On allowing them to stand, perfect subsidence took place, leaving the supernatant water colourless and brilliant. A microscopic examination of the sediment showed it to consist of very fine rock matter, chiefly fragments of quartzite. We then (December 12) determined the "total solids" in the supernatant waters, and obtained the following data:—

	No. 1.	No. 2.
	Parts per million.	
Total solids at 105° C.	16·8	1 6
Solids after ignition	12·0	None.

We thus have proof that the "total solids" of the waters as received consisted almost entirely of *suspended* rock matter. The amounts of *dissolved* mineral and organic matter are extremely small.

The following interesting note on the geology of the vicinity of the Glacier will be read with interest. It is kindly furnished by Mr. R. G. McConnell, of the Geological Survey, Ottawa, a gentleman who for many years has worked on the geology of British Columbia:—

"The rocks in the vicinity of the Glacier are of Cambrian age, and consist largely of bluish quartzites aud fine-grained conglomerates holding pebbles of quartz and felspar imbedded in a hard siliceous matrix. In addition to these, greenish and dark schists of volcanic origin also occur in the neighbourhood.

Chemical Laboratories, Dominion Experimental Farms, Ottawa, March 3, 1899.

NOTE ON THE SPECTRA OF HYDROGEN.

By THEODORE W. RICHARDS.

In a recent paper B. S. Hutton recounts some interesting experiments, which tend to show that Hasselberg's "white spectrum" of hydrogen really belongs to that substance, and not to impurities (Hutton, *Phil. Mag.*, September, 1898, p. 338). One point he was unable wholly to explain—the fact that Cornu (*Journ. de Phys.*, 1886, [2], vol. v., 100-103 and 341-354), and he always obtained a brilliant red four-line spectrum of hydrogen whenever a trace of oxygen was present. The experience recently gained by Professor Trowbridge and the writer upon this subject furnishes the data for an explanation of the matter, and the object of these few words is to remove the uncertainty (*Am. Journ. Sci.*, iii., 117 and 327; or *Phil. Mag.*, 1897, [5], xliii., 135 and 349).

We observed that water vapour under diminished pressure gives the pure red spectrum far more readily than hydrogen itself does, and that when aqueous vapour is mixed with elementary gases it seems usually to be the chosen vehicle for the transport of the electricity. Obviously water must have been formed in Hutton's and Cornu's tubes, and this must have been the source of the red spectrum. The fact that water vapour thus conducts electricity easily may be accounted for by its heterogeneous molecular constitution (compare Volterra, *Ztschr. Phys. Chem.*, 1898, xxvii., 375; also J. Zeleny, *Phil. Mag.*, 1898, [5], xlvi., 120-154, &c.), which is naturally more sensitive to electric stress than the homogeneous structure of the hydrogen molecule. This is only one of the many arguments which go to support the hypothesis that the red spectrum of hydrogen is due to dissociated atoms—or at any rate to the disturbance caused by the act of dissociation, while the white spectrum is due to a compound fracture of polarised particles. Obviously from water only the characteristic lines of atomic hydrogen, not those of molecular hydrogen, could be obtained; and these are obtained so easily that the molecular spectrum of water steps into the background. On the other hand, if the hydrogen is quite dry, as was evidently the case in some of Hutton's as well as in our experiments, the red spectrum requires tremendous heat for its appearance in a state of purity—a circumstance which hypothesis explains simply by ascribing great stability to the polarised molecular structure of the gas.

Randall has recently published a paper in which he recounts his difficulties in obtaining the pure hot red spectrum of hydrogen free from relics of the cool white one (W. W. Randall, *Am. Chem. Journ.*, 1897, xix., 682). Strangely enough he speaks of the presence of aqueous vapour as a possible cause of the existence of the white spectrum, when experimentation would have shown him that the absence of water alone makes this spectrum possible in a state of purity. He seems to have overlooked the fact that a large capacity (10,000 electrostatic units, or more according to circumstances) charged with a very high electromotive force—in other words, great current strength—is necessary in order to provide enough heat to yield the hot spectrum from dry hydrogen, even at its tension of least resistance. This tension varies from one-half to 1 m.m. of mercury, according to the current

strength, a value in any case lower than the tensions employed by him (3 to 8 m.m.). It is very certain that an ordinary Ruhmkorff coil and Leyden jar, such as those used by Randall, could not yield the red spectrum under his circumstances, provided that the gas was dry, as his seems to have been.

It is odd that Randall, while commenting upon a supposed absence of data in our papers concerning the source of our hydrogen, should have himself forgotten to state his mode of generating the gas. His drying train seems to have included sulphuric acid, a dangerous absorbent of water where hydrogen is concerned, but this could not have effected the final result, for the gas whose spectrum he observed had been diffused through platinum. Our hydrogen was prepared by electrolysis from pure dilute hydrochloric acid, was freed from acid by large amounts of potash, and was dried by standing over phosphoric oxide.* It is needless to say that we took all the necessary precautions about sweeping out and filling the tubes, so well known to anyone who has had experience in observing the spectra of gases. One regrets that Randall should have fancied a disagreement between his results and ours, when in reality they are wholly concordant.

In the light of all the facts, and the obvious explanation of Cornu's apparent discrepancy, one can hardly doubt that Hutton and others are quite right in ascribing to hydrogen itself, and not to impurity, the "cool" white spectrum of many lines.—*American Chemical Journal*, vol. xxi., No. 2, February, 1899.

THE ESTIMATION OF TANNIN.

By LEO VIGNON.

I HAVE the honour of presenting a new method for the estimation of tannin based on the following principle:—

Given an aqueous solution of tannin, this substance, to the exclusion of all other bodies which usually accompany it (gallic acid, glucose, &c.), is easily and entirely absorbed by de-gummed silk. It suffices to maintain the silk-tannin mixture digesting for four or five hours at a temperature of 50° C., and to use a large excess of silk with regard to the tannin which should be in dilute solution (5 grms. of silk and about 0·1 grm. of tannin dissolved in 100 c.c. of water).

The tannin thus absorbed may be estimated by several methods:—

a. By Direct Weighing.—By determining the difference of the absolute weights of the silk before and after absorption.

b. By Difference.—By weighing the extract, at 110° C., of the solution of tannin before and after the absorption by the silk.

c. By Difference.—By titrating with permanganate of potash before and after the action of the silk, indigo-carmine being added to the tannin.

In this latter case, the difference found in the permanganate is converted into tannin (gallotannic acid) by applying Neubauer's coefficient of equivalence, confirmed by Sisley (1 c.c. of the solution of permanganate of potash at 3·164 grms. per litre,—

$$\frac{K_2Mn_2O_8}{100},$$

corresponds to 0·004155 grm. of pure tannin.

The process *a* is lengthy, complicated, and not very exact. The second, *b*, is simple and expeditious, and gives sufficiently good results for ordinary practical work. The third, *c*, is the most exact.

I here give the experiments made justifying the method proposed:—

I have made estimations of tannin on samples of sumac and China gall by the new method and by a certain number of the old methods which gave the best results.

1. New method (absorption by de-gummed silk and titration with permanganate).
2. Aimé Girard's method (absorption by violin strings and titration with permanganate).
3. Sisley's method (precipitation of the tannin by ammoniacal acetate of zinc).
4. New method (absorption by silk and weighing the extracts).
5. Aimé Girard's method (absorption by violin strings and weighing the extracts).

Method.	Tannin found per cent of material.	
	Sumac. 20 grms. of leaves, 1000 c.c. water.	Gall. 10 grms., 1000 c.c. water.
1	16·34	52·42
2	16·34	52·42
3	16·27	52·03
4	16·40	52·65
5	16·50	53·10

These results are very concordant within the limits of commercial analysis.

The method based on the use of de-gummed silk should be applied in the following manner:—

Silk.—The de-gummed silk is washed and rinsed in distilled water. It can be easily prepared by treating 20 grms. of raw silk in two successive baths of 500 c.c. of distilled water containing 50 grms. of white soap. Each bath should be used, boiling for thirty minutes. The silk is smoothed in the soap bath, wrung out after the first, and rinsed and thoroughly wrung again in distilled water after the second bath, to remove all the soap. For each estimation of tannin, we employ 5 grms. of silk (weighed to 0·01 grm.).

Solution of Tannin.—We weigh out 3 grms. of tannin in ether solution (containing about 86 per cent), 10 grms. of rich materials (gall nuts at 50 per cent), 20 grms. of medium material (sumac, oak-bark), and exhaust methodically with warm distilled water at about 60° C., filter, and make up to 1000 c.c. with distilled water measured at 50° C.

Permanganate of Potash.—The solution should contain 3·164 grms. $K_2Mn_2O_8$ per litre, and be checked with oxalic acid or ferrous sulphate.

Solution of Indigo.—Twenty grms. of superfine paste of indigo-carmine (20 per cent in 1 litre of water).

Estimation.—To estimate the tannin in a China gall-nut, 10 grms. of the gall-nut are exhausted with 1000 c.c. of water (A); 50 c.c. of A are diluted to 250 c.c. (B).

Titration of the Indigo by the Permanganate.—In a two-litre porcelain dish we place 1 litre of distilled water, 50 c.c. of the indigo solution, and 10 c.c. of pure sulphuric acid. We then add, by means of a burette with a glass tap, of 50 c.c. capacity, divided into tenths of a c.c., the permanganate solution (1 drop a second), stirring regularly until the complete decolouration of the indigo—say, 22 c.c. of permanganate for each 50 c.c. of indigo.

Titration of the Tannin in the presence of Indigo.—Take 1 litre of distilled water, 50 c.c. of indigo, 50 c.c. of tannin, and 10 c.c. of sulphuric acid; we find for decoloration:—

Permanganate	40·05 c.c.
From which we deduct for the indigo ..	22·00 ,,
That is, for the tannin	18·05 ,,

Absorption of the Tannin.—To 100 c.c. of the liquor B we add 5 grms. of de-gummed silk in an emery pounce-box of 250 c.c. capacity, and keep it in the oven at 50° for five hours (*not more*), while stirring from time to time. After cooling, the tannic liquor in which the silk is soaking is again titrated with permanganate.

* Compare *Am. Journ. Sci.*, iii., 331; a paper published three months before the date of Randall's. Hutton also overlooked this paper.

Titration of the Liquor after Absorption.—Take 1 litre of distilled water, 50 c.c. of the exhausted solution, 50 c.c. of indigo, and 10 c.c. of sulphuric acid; we found:—

Permanganate	26·80 c.c.
From which we deduct for the indigo ..	22·00 ,,
	4·80 ,,

The tannin absorbed by the silk corresponds to 18·05 − 4·80 = 13·25 c.c. permanganate. We thus deduce for the percentage of tannin (counted as gallotannic acid) present in the sample—

$$13{\cdot}25 \times 1000 \times 0{\cdot}004155 = 55{\cdot}05.$$

We have already stated that the operation might be simplified—though losing a little of its exactness—by determining the extract at 110° before and after absorption and calculating the tannin by difference.

The method proposed presents the following advantages:—The material for absorbing the tannin (de-gummed silk) is easily obtained in a state of purity. It is homogeneous, regular, and unchangeable; it is weighed and manipulated with great ease. Violin strings, on the contrary, require rather a long preparation. Powdered skins are irregular, and give up soluble organic matter to water, and are not at all to be depended upon. The absorption by silk is effected in five hours at 50°, while the violin strings and skin powder can only be used cold and take about thirty hours. Finally, the coloration of the silk after absorption enables us to estimate comparatively, to a certain extent, the coloration of the tannin; this indication is extremely useful in dyeing and tanning.—*Bull. Soc. Chim.*, Series 3, xix.-xx., No. 22.

A NEW METHOD FOR THE PREPARATION OF CHLOROPLATINITE OF POTASSIUM.

By M. VÈZES.

I. Of all the platinum compounds the chloroplatinite of potassium, $PtCl_4K_2$, is the one which is of the greatest interest from the point of view of its applications; it is, in fact, in the form of chloroplatinite of potassium that platinum is used by photographers for producing permanent positive proofs known as "platinotypes," the demand for which is constantly increasing. Now the methods used up to the present for the preparation of this salt are far from having the simplicity and economy of manufacture necessary to a truly commercial article.

Chloroplatinite of potassium can be obtained either directly from metallic platinum or from the chloroplatinate. In the first case the method most generally used is that proposed by Claus. The metal is transformed into chloroplatinic acid by solution in aqua regia, evaporation to dryness, and re-solution in water slightly acidulated with hydrochloric acid: this acid is reduced in warm dilute solution by a current of sulphurous acid gas, which changes it into chloroplatinous acid; finally the solution obtained, to which an equal quantity of chloride of potassium has been added, gives, on cooling, the crystallised chloroplatinite.

This method is, as can be seen, long and complicated, and, further, the reduction of the chloroplatinic acid by the sulphurous acid gas is a very delicate operation to perform properly, an excess of sulphurous acid being able to transform the chloroplatinous acid into difficultly destroyed platosulphurous compounds, so that constant attention and frequent tests are necessary so as to stop the current of gas at the right moment.

Besides Claus's method we may mention two others, which only differ in the method adopted for changing the chloroplatinic acid into chloroplatinous acid. In the method described by Magnus (*Ann. Chim. Phys.*, Series 2, vol. xl., p. 110) the solution of chloroplatinic acid is evaporated to dryness, and the residue heated to a temperature of about 350°. Water, hydrochloric acid gas, and chlorine are given off, and platinous chloride, $PtCl_2$, remains, insoluble in water, but soluble in warm hydrochloric acid, giving a solution of chloroplatinous acid. But, as Pigeon has shown (*Ann. Chim. Phys.*, Series 7, vol. ii., p. 446), this decomposition of the chloroplatinic acid by heat is not effected completely except *in vacuo*, in the presence of melted potash and at the temperature of boiling mercury; without these precautions, which are almost impracticable in commercial operations, the return of chloroplatinite is but mediocre.

Finally, Pigeon's method (*Compt. Rend.*, cxx., 681) consists of saturating chloroplatinic acid with carbonate of barium, and then heating the solution obtained on the water-bath with an exactly equivalent quantity of dithionate of barium. This then passes to the state of sulphate, which is precipitated, and the filtered liquor does not contain anything but chloroplatinous acid with an excess of hydrochloric acid. This beautiful method gives excellent results, but it has the double inconvenience, from the industrial point of view, of requiring very exact weighings, and also the use of a relatively expensive salt.

II. On the other hand, chloroplatinite of potassium can be also obtained from the chloroplatinate, $PtCl_6K_2$, by the direct reduction of this salt. The methods of preparation based on this principle are *à priori* the most advantageous, considering that it is in the form of chloroplatinate of potassium* that the platinum is finally found in most of the operations to which these compounds may have to be submitted; the platinum residues are, in fact, always largely composed of chloroplatinate, in the same way that those of silver are generally chloride.

It is evidently of great advantage to be able to convert the residues directly into chloroplatinite, without passing through the metallic state, in the same way that it would be very convenient to convert silver residues directly from chloride to nitrate without first bringing them to the metallic state.

Two methods have been proposed for the direct conversion of chloroplatinate of potassium into chloroplatinite. Böttger (*Journ. f. Prakt. Chem.*, vol. xci., p. 251), treated the solution of chloroplatinate with a current of sulphuretted hydrogen, which reduces a part of the salt to the state of chloroplatinite, but at the same time precipitates the major part of it in the state of sulphide; the return of chloroplatinite is therefore not very great. Thomsen (*Journ. f. Prakt. Chem.*, Series 2, vol. xv., p. 295), heats the solid chloroplatinate with a little water and an excess of cupreous chloride, which reduces it while passing to the state of cupric chloride. The solution thus obtained, separated by filtration from the excess of cupreous chloride and unreduced chloroplatinate, deposits on cooling crystals of chloroplatinite. But these crystals always retain a little copper, the separation of which requires several washings with alcohol; further, the return of chloroplatinite is not great. Groger (*Zeit. Angew. Chem.*, 1897, p. 152), has modified Thomsen's method, with regard to increased returns, by adding to the mixture powdered zinc; he thus obtained 76 per cent of the theoretical yield. But it is evident that this addition does not constitute an improvement from the point of view of the purity of the product obtained.

It can be seen from the foregoing what improvements are necessary in the commercial preparation of chloroplatinite of potassium; a simple method of reduction of the chloroplatinate, not requiring expensive reducing agents, and not requiring special precautions, and giving a good return of a product perfectly free from foreign metals.

III. We have recently shown how the chloroplatinate of potassium can be transformed into plato-oxalate by the

* The platinum residues sometimes also contain chloroplatinate of ammonium; but it is not difficult to transform this into a potassium salt by boiling with potash.

action of an excess of neutral oxalate of potassium, in dilute, boiling solution,—

$$PtCl_6K_2+3CO_2K.CO_2K=Pt(CO_2.CO_2)_2K_2+2CO_2+6KCl.$$

On the other hand the plato-oxalate thus obtained can be easily transformed into chloroplatinite by the action of an excess of hydrochloric acid. These two reactions together thus constitute a process for the transformation of the chloroplatinate of potassium into chloroplatinite, a process fulfilling, at least partly, the theoretic conditions indicated at the end of the preceding paragraph.

This process, it is true, is not absolutely direct, since it requires the production during its operation of the plato-oxalate, which must be crystallised and separated from its mother liquor before being subsequently transformed into chloroplatinite. Further the slight solubility of the chloroplatinate in water, even when boiling, makes it difficult to effect the transformation of notable quantities of this salt into the plato-oxalate in a single operation.

IV. These inconveniences may be entirely avoided by applying an important modification, which has only recently been discovered, to the operation. This reaction (the transformation of the chloroplatinate into the plato-oxalate) may be considered to take place in two phases; in the first, the chloroplatinate is reduced by a molecule of the oxalate, from which all the carbon is eliminated in the form of carbonic acid :—

$$PtCl_6K_2+CO_2K.CO_2K=PtCl_4K_2+2CO_2+2KCl;$$

in the second, the chloroplatinite formed is transformed into plato-oxalate by exchange with the two other molecules of oxalate—

$$PtCl_4K_2+2CO_2K.CO_2K=Pt(CO_2.CO_2)_2K_2+4KCl.$$

From this it results that we ought to be able to effect the direct reduction of the chloroplatinate to chloroplatinite by producing the first phase of the preceding operation only; that is to say, by using only one molecule of oxalate for one molecule of the salt.

This has been verified by experiment; and from it has been evolved a method for the preparation of the chloroplatinite fulfilling perfectly all the theoretical conditions indicated above. In particular it requires three times less oxalate than the preceding process, and further it can easily be applied on a large scale, as it will no longer be necessary to use a quantity of water sufficient to dissolve all the chloroplatinate employed in the operation.

The method of working will therefore be as follows:—The chloroplatinate is suspended in a quantity of water, insufficient to dissolve it even when warm (1 litre per 100 grms. of chloroplatinate, for example; there would be no inconvenience in even reducing this quantity of water). We add one molecule of neutral oxalate of potassium for each molecule of the salt (say 37 grms. of crystallised oxalate, $CO_2K.CO_2K+H_2O$, per 100 grms. of chloroplatinate), and heat to boiling. The oxalate dissolves and reacts on the dissolved part of the chloroplatinate; it gives off carbonic acid gas, and the solution, at first a deep yellow, becomes red, The chloroplatinate thus gradually dissolves, passing to the state of chloroplatinite, and finally, after the lapse of several hours, the whole is dissolved: the deep red liquor obtained leaves on cooling perfectly pure chloroplatinite. The weight of the crystals thus obtained by the single operation naturally depends on the more or less concentrated condition of the liquor during ebullition; with a convenient concentration it may be more than 80 per cent of the theoretical weight of the chloroplatinite corresponding to the chloroplatinate employed. By the addition of alcohol to the mother liquors it is easy to precipitate almost the whole of the remainder of the salt.

To sum up, the preparation of chloroplatinite of potassium may be easily and economically effected from chloroplatinate of potassium by the direct reduction of this salt, held in suspension in boiling water, by means of an equivalent quantity of neutral oxalate of potassium. —*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 22.

NEW METHOD FOR THE PREPARATION OF CÆSIUM.*

By HUGO ERDMANN and A. E. MENKE.

WINKLER (*Ber. d. Chem. Ges.*, xxiii., 53), tried to reduce cæsium carbonate with metallic magnesium, in both glass any porcelain tubes in a current of hydrogen. He, however, obtained no cæsium. Beketoff (*Bull. Acad. Petersburg*, iv., 247), states that it can be obtained in small quantities by the electrolytic reduction of the cyanide; he also acted on the hydrate with aluminum, but the yield was poor. In 1894 he made a small amount by acting on cæsium alum with metallic magnesium (*Proc. Russ. Phys. Chem. Ges.*, 1894). We made a great many experiments with a view to improving these processes, but finally found that a different method worked remarkably well, and if the directions are exactly followed it is absolutely free from danger. We found that by heating cæsium hydroxide with magnesium powder in a red-hot tube through which passed a current of hydrogen, we could obtain nearly the theoretical amount of cæsium. Inasmuch as we always commenced with cæsium alum, and as that is the cheapest and most available salt to begin with, we will give all the details of the method that we finally found to be the best. The cæsium alum should be first converted into cæsium sulphate. It is not advisable to convert it directly into cæsium hydroxide on account of the fact that too much water is required to dissolve the cæsium alum, and also because cæsium hydroxide absorbs carbon dioxide very rapidly. In order to convert cæsium alum into cæsium sulphate the following reaction can be used:—

$$2CsAl(SO_4)_2.12H_2O+3Ba(OH)_2.8H_2O=$$
$$=Cs_2SO_4+2Al(OH)_3+3BaSO_4+48H_2O.$$

Dissolve the cæsium alum in as small a quantity of boiling water as possible (it is more convenient in all operations connected with cæsium to use casseroles rather than dishes or beakers), and in a separate casserole dissolve the crystalline barium hydroxide; when both are in solution, mix the two and filter rapidly with a good pump; a Buchner funnel can be used in this operation to great advantage. The filtrate if slightly alkaline, due to an excess of barium hydroxide, should be treated with carbon dioxide for a few minutes and quickly re-filtered. It can now be either evaporated to dryness or crystallised. The next step is to convert the cæsium sulphate into cæsium hydroxide.

$$Cs_2SO_4+Ba(OH)_2.8H_2O=2CsOH+BaSO_4+8H_2O.$$

The sulphate is quite soluble in hot water, and as small a quantity of the solvent as possible should be used. The barium hydroxide should also be separately dissolved in a very small quantity of water. When both are in solution mix and filter with a suction-pump and Buchner funnel. The filtrate is rapidly evaporated to dryness in a silver crucible and then fused; it should now be poured into a silver dish so that it will make a thin brittle cake of cæsium hydroxide, which must not be exposed to the air longer than is absolutely necessary; it is quickly broken, transferred to a warm dry bottle, and weighed; then put into a hot porcelain mortar, broken into small pieces about half the size of a pea, and mixed with one-half of its weight of magnesium powder (the magnesium powder must be previously heated in a current of hydrogen to get rid of the fat with which it is always mixed); the mixture is then quickly dropped into a clean, dry, rust-free malleable iron tube of the following dimensions: 1 metre long, 15 m.m. diameter, 3 m.m. thick, and 15 c.m. from the end it is bent to an angle of about 125°. In order to keep the mixture in the tube a small bundle of clean piano wire irregularly twisted together is forced into

* Read by title before the New York Meeting of the American Chemical Society, December 28, 1898. From the *Journal of the American Chemical Society*, vol. xxi., No. 3.

the tube down the long part to the angle, before dropping in the mixture. In filling the tube it is best held inclined. The tube is now laid in a slightly inclined combustion furnace, to aid the flow of the liquid metal and quickly connected to a Kipp hydrogen generator. The hydrogen must be passed through permanganate solution in order to oxidise hydrogen arsenide, and then thoroughly dried by sulphuric acid and phosphoric anhydride; the bent end of the tube is immersed in liquid paraffin to the depth of about 2 c.m. It is advisable to have the paraffin in a casserole about 7½ c.m. in diameter. To begin the distillation, light the burner farthest away from the mixture (the tube should never be more than one-third full), and allow hydrogen to pass through at the rate of about 40 bubbles per minute. When the temperature has risen as high as one burner can produce, light the next, but do not turn on full pressure immediately; this process must be continued, burner by burner, until reaction begins. This is readily marked by an increase in the speed of bubbling through the paraffin. If the bubbles come faster than 80 to 100 per minute, turn out the last lighted burner and remove the tile over the tube. Bubbling will now gradually cease, due to the probable formation of hydride of cæsium, decomposed at high temperatures; consequently the hydrogen pressure must be increased until gas comes through the paraffin. When the back suction is relieved the hydrogen stream can be restored to its normal rate. This operation must be continued until all the burners are lighted and the temperature is full red. The angle piece of the tube, which should be as close to the furnace as possible, is now heated by a powerful Bunsen burner, and constantly struck with a piece of iron. The metallic cæsium which has distilled into this part of the apparatus, will be liquefied, and will trickle down under the paraffin, collecting in silvery drops. The cæsium comes out of the tube at the very end of the process and not before. If the foregoing directions are closely followed the whole operation can be accomplished in four hours without the slightest difficulty or danger. Explosions only occur when the tube is heated too rapidly, and not sufficient attention paid to the pressure regulation. It is evident from the result of these experiments that Winkler was mistaken in stating that it is impossible to obtain cæsium from its compounds by the aid of magnesium. We made cæsium in quantity by our method and are now studying its physical properties.

A REVISION OF THE ATOMIC WEIGHT OF NICKEL.*

Second Paper.—The Determination of the Nickel in Nickelous Bromide.

By THEODORE WILLIAM RICHARDS
and
ALLERTON SEWARD CUSHMAN.

In a recently published investigation upon the atomic weight of nickel we gave three series of results, depending upon the ratios of silver and of argentic bromide to nickelous bromide (*Proc. Amer. Acad.*, xxxiii., 97). These led us to the conclusion that the atomic weight in question could not be far from 58·69 if oxygen is 16·000. Since, however, no single method is ever convincing, and since the results above mentioned did not represent all that might be done even with one method, it was evidently advisable to pursue the matter to a more definite conclusion. Accordingly, we determined to continue the work with a two-fold object in view; first, to study further the preparation of pure material, and secondly, to complete the analysis of nickel bromide in such a way as to *determine directly the amount of nickel as well as the amount of bromine in the salt.* No surer test of a quantitative result than such a complete analysis is known. The careful study of all the conditions and results has led us to the conclusion that the preparation of pure nickelous bromide is an unusually difficult problem; but the problem has been so nearly solved that we know exactly the precautions and corrections necessary to make this substance serve as an accurate basis for the determination of the atomic mass of nickel. In the light of this later knowledge we find that the results of the last paper need a slight correction, but it is satisfactory to note that the change amounts to not much over one unit in the second decimal place of the atomic weight.

While carrying out the work, we had continually in mind the various controversies which have arisen over the atomic weights of nickel and cobalt; and feeling that the "Gnomium" question raised by Krüss and Schmidt had never been conclusively laid at rest, we naturally dwelt especially upon it. Unfortunately, one cannot enter into a discussion of this subject without directly antagonising many views which have been expressed on one side or the other; but of course the following results are recorded solely in the interests of truth, without controversial bias.

The balance and weights used in the work described were the same as those described in the former paper. The weights were re-standardised, with results very similar to those found a year before. All weighings of nickelous bromide were reduced to the vacuum standard by the addition of 0·114 milligrm. per grm. to the observed weight. The specific gravity of nickel (about 8·7) is so near the specific gravity of brass (8·4) that the correction of the nickel to the vacuum standard is less than one part in a hundred thousand, hence it may be omitted.

Experiments concerning the Purity of the Materials.

The purification of our nickelous material has already been described at length (*Proc. Amer. Acad.*, xxxiii., 102). Most of the work described below was done with nickel which had been purified by Mond's process and many subsequent operations (Sample III.), but two analyses were made with a somewhat less pure sample (No. II.) made from commercial material. (See *Proc. Amer. Acad.*, xxxiii., 102 and 105). Since we had proved that further protracted treatment produced no effect on the combining weight, evidently these specimens were quite pure enough for our purpose.

Krüss and Schmidt used glassware in their preparation work, therefore it seemed worth while to make an exact observation of the well-known danger involved in this practice. To this end two very carefully treated specimens of spongy nickel were prepared, one having been made wholly in platinum, and the other wholly in the best Bohemian glass, which had been thoroughly steamed. The former of these preparations, which was supposed to be absolutely pure, left upon sublimation as bromide in a stream of bromine vapour only a very minute siliceous residue. The specimen of nickel which had been prepared in glass vessels was totally different in appearance from the one prepared in platinum; instead of being metallic and coherent, it was black and powdery. Upon the conversion of about 10 grms. of this dark powder into nickelous bromide, a beautifully iridescent, voluminous residue, weighing about 5 milligrms. and consisting mainly of silica, was left in the boat. Evidently this silica had prevented the cohering or "sintering" of the metal during its original reduction from the oxide, and hence caused the pulverised state of the impure metal—a fact which is interesting as showing the great change in properties produced by a small amount of impurities.

These two experiments emphasise the well-known facts that glass is wholly unsuitable for accurate work, and that material prepared even in platinum is extremely difficult to render wholly free from silica, unless it is vapourised (compare Stas's "Untersuchungen," Aron-

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, Vol. xxxiv., No 13, February, 1899.

stein, pp. 269 and 279). While, however, our purest *nickel* sometimes contained traces of silica, the *bromide* prepared from it by sublimation was undoubtedly as free as possible from this impurity. Further light upon this question will be given in a following paper upon cobalt.

Although a possible contamination with silica was thus little to be feared, some other constituents of glass or porcelain were much more dangerous. All the material actually used in our analysis had been prepared wholly in platinum vessels at every stage excepting at the very end, when it had been sublimed in a porcelain tube. Obviously this tube might be attacked by the hot mixture of hydrobromic acid, bromine, and nickelous bromide vapour; but since nothing beside sodic bromide would probably sublime with the nickelous salt, and the "equivalent" of sodic bromide is almost equal to that of nickelous bromide, the slight impurity could produce no important effect upon our last year's work. This was realised at the time; and the discovery of the presence or absence of this error was one of the prearranged objects of the present paper. Since the work recorded below was completed, Professor Winkler, by a kind personal letter as well as by a recent article, wisely called attention to this flaw; and it will be seen that his objection had been both substantiated and answered before he wrote about it.

The easiest method of detecting sodic bromide in nickelous bromide is obviously to reduce the latter and then to extract the former with water from the spongy metal. Moist hydrogen easily divorces the halogen from its none too stable metallic union at a temperature of not much over 300°, at which temperature sodic bromide is essentially non-volatile. In this way repeated experiments showed that all our nickelous bromide had contained on the average not far from one-tenth of 1 per cent of sodic bromide. The particulars concerning the determination of this serious impurity naturally form an essential point in the method of analysis of the nickel salt, hence they will be found later under that head. The presence of an unreduced bromide was first detected by Mr. Baxter in the course of his work on cobaltous bromide, and some interesting details involved in its discovery will be recorded in the paper upon that subject. The amount present varied with the temperature used in the sublimation, but was otherwise surprisingly constant. The concurrent sublimation of the two salts is undoubtedly similar to the distillation of organic substances with steam, sodic bromide possessing a small constant vapour-tension at the constant temperature of about 900° used in the sublimations.

After the completion of a series of reductions of nickelous bromide containing this impurity of sodic bromide, a final attempt was made to obtain the salt of nickel in a state of absolute purity. We expected that platinum would be attacked by the mixture of bromine vapour, hydrobromic acid, and nickelous bromide, which exists in the red-hot tube during the sublimation of the salt, but platinum is the last resort in cases of this kind. In order to sacrifice as little of the precious metal as possible in our desperate experiment a large porcelain tube was lined with platinum foil,* and inside of this was placed a platinum boat containing the metal to be converted into bromide. In each of two separate specimens of nickelous bromide made in this apparatus merely a trace of sodium was found, but unfortunately enough platinum was present to render the results valueless. They are not included in the tables below. Only a small strip of the foil was injured, the very hot parts and the cool parts being alike untouched. After these experiments we abandoned the attempt to prepare absolutely pure nickelous bromide, and returned to the use of the porcelain tube for the sublimations; for sodium is an impurity much more easily weighed than platinum, under the circumstances. The only method of obviating the difficulty would have been to use a tube of nickel for the sublimation; but the obtaining and moulding of a large amount of the metal in a perfectly pure state promised to be so troublesome that we have not yet attempted this improvement.

The arrangement for supplying and purifying the large volumes of hydrogen needed in this research was gradually evolved from the simple form used in the first experiments to an elaborate piece of apparatus which will be described in detail in the paper upon cobalt.

The preparation of bromine and of the other materials has been described in sufficient detail in other papers (*Proc. Amer. Acad.*, xxxiii., 106, *et seq.*), so that no further words need be wasted upon these points. It is almost unnecessary to state that in these simple operations no loophole was left open through which an error might creep in to destroy the value of the more difficult undertaking before us. We are indebted to the Cyrus M. Warren Fund for Chemical Research in Harvard University for some of our more expensive pieces of apparatus.

The Method of Analysis.

At first many attempts were made to determine nickel by electrolysis, with the hope that nickelous bromide might be analysed in this simple and direct fashion. In order to test the method, weighed amounts of the purest spongy metal were dissolved and re-precipitated electrolytically. The spongy metal had been prepared by boiling the purest platinum-made ammonio-nitrate with much water, igniting and reducing the precipitate with pure ammonia, and heating the metal in a vacuum. The weight of nickel deposited by electrolysis always exceeded that of the pure nickel taken, hence the electrolytic method was abandoned as unsuitable for work of the highest accuracy. The excess of weight, which was noticeable even when the film was heated to 120° before weighing, and often exceeded two-tenths of 1 per cent when it was dried at 50° after the method of Winkler (*Zeit. Anorg. Chem.*, iv., 22), was traced to inclusion of mother liquor between the film and the dish, and to the probable presence of occluded hydrogen in the nickel (Raoult, *Comptes Rend.*, lxix., 826; Böttger, *Dingler's Polytech. Journ.*, 1871, cci., 80). Since the deposit was beautifully metallic and coherent in appearance, one might well have expected a better result. It is possible that these observations may help to explain Winkler's high values for the atomic weight of nickel and cobalt, since he used the electrolytic method. On the other hand, the *spongy* metal which had been used in our experiments was probably purer than that prepared in any other way, for solid impurities had been rigorously excluded, and the traces of gas present had been pumped out.

These preliminary experiments showed that the best method of determining the amount of nickel in the bromide would be to reduce it in a stream of hydrogen, provided that the reduction could be accomplished without the loss of any of the bromide by volatilisation. Following in the footsteps of Mr. Baxter's work with cobalt, it was found that moist hydrogen answered the purpose; for the temperature at which the reduction takes place is so low that no trace of nickel was found outside of the boat which originally contained the bromide, if a rapid current of the gas was maintained. It is obvious that according to the law of mass-action, the presence of a large proportion of hydrobromic acid resulting from the reduction would tend to prevent the desired reaction, and hence to facilitate the undesired sublimation; therefore a large excess of hydrogen must be present. Of course the hard glass tube used for this process was always afterwards treated internally with nitric acid, and the liquid was examined with minute care for traces of nickel.

The nickelous bromide to be analysed was contained in a platinum boat, and the method of drying and weighing it was in every respect the same as that described in detail in the previous paper upon this subject. After having been weighed, the boat was carefully placed in a hard glass tube, in which the bromide was cautiously re-

* This idea was suggested by Professor H. B. Hill. Compare also Penfield, *Zeit. Anorg. Chem.*, vii, 22.

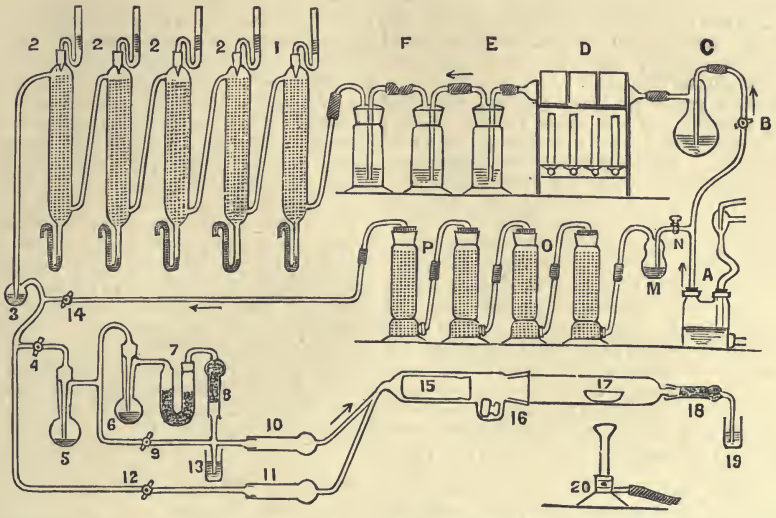


Fig. 1.—Apparatus for Igniting Nickelous Bromide in any Desired Mixture of Gases. The use of rubber was confined to the first part of this train, where it could do no harm (A B C D E F and A M N O P).

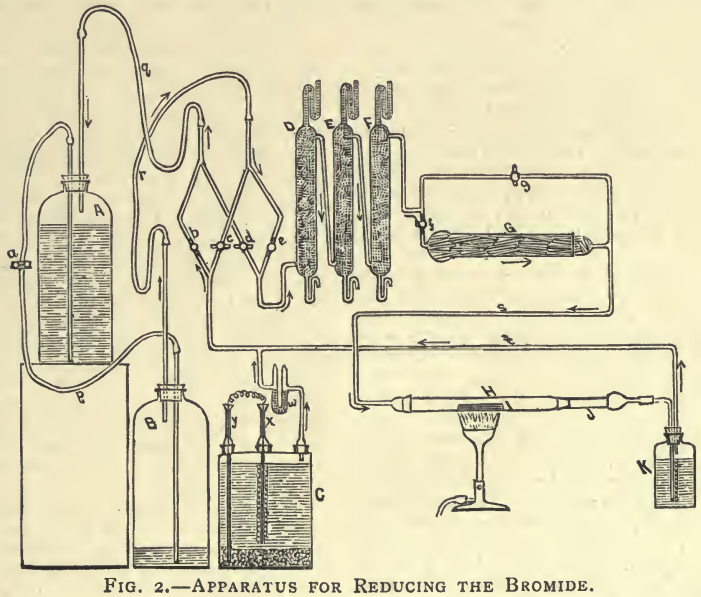


Fig. 2.—Apparatus for Reducing the Bromide.

duced to the metal. When the reduction was completed and the apparatus had just cooled, the boat and its contents were returned to their weighing bottle, where they were enclosed in an atmosphere of dry air. The weight of the residue was found after half an hour, and then at the end of many hours. Since the boat was cool before having been introduced into the bottle, two successive weighings thus made never differed from one another by amounts beyond the limit of error of weighing. Spongy nickel evidently does not oxidise in dry air.

It is obviously a matter of great importance to discover whether or not the material prepared in this way contains weighable amounts of occluded hydrogen. According to the experiments of Neumann and Streintz (*Monatshefte für Chem.*, 1891, xii., 640; *Ber. der. d. ch. Gesell.*, 1872, xxv.), who worked with reduced metals, 2 c.c. of the gas were occluded by each grm. of spongy nickel. This amount would alter the observed atomic weight by only about the fortieth of 1 per cent; but since we are aiming at even greater accuracy, the matter should evidently be probed to the bottom.

In the first place, carefully weighed nickelous bromide dissolved from one of the analyses recorded below was heated in a Sprengel vacuum at perhaps 550°. Care was taken for fear of losing some sodic bromide a higher temperature could not be employed. No appreciable loss of weight occurred and no gas was evolved during this process, which was repeated with several specimens; hence there seemed to be good reason to believe that no hydrogen was occluded by the metal in our experiments. In order to prove the matter, 1½ grms. of spongy nickel reduced from the bromide and allowed to cool in hydrogen was oxidised by heating in a current of dry air, which was subsequently passed over red-hot cupric oxide, and through a carefully

weighed tube containing phosphoric oxide. Since the absorption tube did not gain in weight, no water could have been formed during the combustion, and hence no hydrogen could have been occluded.

Treated in exactly the same way, 4 grms. of nickel prepared by the reduction of the *oxide* yielded about 3 milligrms. of water or about half the amount found by Neumann and Streintz. This agreement is sufficient to show that these investigators were not mistaken in their conclusions, and that the permeability of nickel is enormously modified by minor circumstances.

Is the presence of the sodic bromide, otherwise so objectionable, the agency which prevents the occlusion in our case, or does the volatility of nickelous bromide allow its metal to be deposited in a form more coherent than that remaining from the oxide? The attempt to answer these questions experimentally would be far from uninteresting, but it is sufficient for the present purpose to prove in the manner described above that nickel treated as we have treated it in the following determinations does not occlude an important amount of hydrogen, and does not oxidise in dry air. Confirmatory evidence will be found in the paper upon cobalt which follows.

Before it was possible to use the data thus obtained for the calculation of the desired atomic mass, the weight of sodic bromide existing as impurity within the spongy metal must obviously be found. Accordingly the residue was digested with successive portions of pure water in a platinum dish, and the bromine in the filtrates was precipitated and weighed as argentic bromide. Since the spongy metal (after slow solution in very dilute nitric acid in a platinum dish) was found to contain no bromine, it is safe to infer that all the soluble impurity had been leached out by the water. This process was repeated with every analysis, the result being always the same. From the weight of argentic bromide thus obtained, the weight of the impurity of sodic bromide was calculated, and when this quantity was subtracted from both the original weight of the nickelous bromide and the weight of the spongy metal, data suitable for the calculation of the atomic mass were obtained.

In order to show that this method of correcting the results is really exact, it is necessary to prove, first, that no impurity other than a bromide remains behind in the nickel, and secondly, that no impurity beside sodic bromide is dissolved by the water. The first point has been already partially considered; we have shown that silica at least was absent (see *ante*). Since silica was the only non-volatile and insoluble acid likely to have been present, and all the bromine had been dissolved out by water, the only probable impurities were other metals capable of being reduced from their bromides by hydrogen. But these, even if they had been present in unsuspected and undiscoverable traces, could have exercised no appreciable effect upon the atomic weight unless their equivalents were widely different from that of nickel. Hence this possibility of error need cause no anxiety. Finally, it has been already stated that no weighable amount of hydrogen was ever found in the metal; hence we are justified in the assumption that the washed out nickel is a safe material upon which to base the calculation of the atomic mass in question.

The question as to the purity of the sodic bromide in the wash-liquors was a matter less easily settled. Careful qualitative and quantitative analysis of the liquid were alone capable of deciding the point, and with only infinitesimal amounts of material such elaborate examination was difficult. To make a very long story short, nothing was found in any of the wash-waters beside sodium, bromine, nickel, and in some of the earlier analyses traces of sulphuric acid. This last impurity may have crept in from the air during the evaporation of the aqueous solutions, or possibly from the towers used for drying the nitrogen and air. In the later analyses sulphuric acid was not used in these towers, and was proved to be absent from the nickelous bromide. As its amount was in any case very small, we felt justified in neglecting it as one neglects an infinitesimal of the second order in the course of mathematical reasoning.

On the other hand, the amounts of nickel in the wash-waters were distinctly weighable, and not to be overlooked. That it was nickel, and not a new metal, there could be no room for doubt, for it gave a black sulphide and a green sulphate, the characteristic pink colouration with potassic thiocarbonate, as well as a beautiful rose-coloured flame test, which we have found to be characteristic of nickelous halides. Since the nickel salts are much more easily reduced than those of cobalt (see the next paper), it is harder to obtain a satisfactory flame test in the former case than in the latter. Only when both salts and gas are *dry*, and the vaporisation proceeeds in the inner flame, are the best results to be obtained. We have found no reference to this flame reaction of nickel halides in chemical literature (Vogel, *Spectral Anal. irdis. Stoffe.*, pp. 246, 262), and one cannot but believe it to have been unknown to Krüss and to Winkler at the time of one of their disputes.*

(To be continued).

NOTICES OF BOOKS.

Examination of Water (Chemical and Bacteriological). By WILLIAM P. MASON. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1899. Pp. v.—135, 12mo. Illustrated.

THE author of this convenient little handbook assumes that the student has a knowledge of ordinary quantitative analysis, and therefore gives mere suggestions for the determination of the mineral matters present in water, and develops more fully items properly lying within the scope of a sanitary examination. In the Introduction Dr. Mason refers to some popular misconceptions concerning the analysis of potable water, and says it should not be looked at from the same point of view as the analysis of an iron ore, because the results reported in the two cases are not analogous, nor equally capable of interpretation. He points out the necessity for the chemist who is analysing a water used for drinking purposes to know its history, its geographical situation, &c. The amount of chlorine found, for example, should be compared with "normal chlorine" of the region whence the sample is taken: this point is illustrated by two maps, one of the State of Massachusetts (prepared by the Board of Health), and one of Connecticut, showing the distribution and quantity of chlorine in the potable waters of the two commonwealths.

The volume gives simple and clear directions for sampling the water to be examined, and for testing its hygienic value. He favours Griess's second method for determining nitrites, the picric acid method of estimating the nitrogen present as nitrates, and Wanklyn's albumenoid ammonia process. Following the description of each analytical process is a paragraph headed with the unusual word "Comparates," which contains sundry data and the opinions of various authorities with reference to the method and the results. This feature will assist the laboratory analyst to make comparisons of the water under examination with others good or bad. A table shows that the rain-water freest from nitric nitrogen falls in the interior of Scotland, and that containing the most in Paris.

The chapter on bacteriological examination is rudi-

* Kruss and Schmidt, *Zeit. Anorg. Chem.*, li., 249; Winkler, *Zeit. Anorg Chem.*, iv., 17. Krüss observed the appearance of a pale rose-coloured flame during the ignition of his nickel in a Rose crucible in hydrogen, accompanied with a loss of weight. If the hydrogen was *dry*, and especially if, as is often the case, it contained traces of hydrochloric acid, minute traces of nickelous chloride might have been sublimed and have caused this phenomenon, which Krüss ascribed to "gnomium" and Winkler ascribed to potassium. This question is worthy of further attention.

mentary, no attempt being made at ultimate differentiation; Miquel is often cited as authority. Instructions are given for counting the colonies of bacteria and testing for *B. coli communis*.

It is interesting to note that bacteria have been exposed for several hours to liquid air without destroying them; but if the water is heated under pressure to 115° C. for 45 minutes the bacteria are absolutely destroyed. Ordinary boiling of water for half an hour will destroy 99 per cent of the bacteria.

The book has an Index. H. C. B.

Manual of Clinical Chemistry. By Elias H. Bartley. Philadelphia: P. Blakiston's Son and Co., 1012, Walnut Street. 1899. Pp. vi.—150. 12mo. Thirty-three Illustrations. Cloth.

The author of this little manual holds degrees and offices that indicate some of his qualifications for instruction in the subject of which it treats; he is "B.S., M.D., Ph.G., Professor of Chemistry and Toxicology in the Long Island College Hospital; Dean and Professor of Organic Chemistry in the Brooklyn College of Pharmacy." His "Text-book of Medical and Pharmaceutical Chemistry," now in its fifth edition, is widely and favourably known to students in Medical Colleges, pharmaceutists, and physicians; the work under review is made up of the last eighty-three pages of that "Text-book," to which have been added notes on urinary diagnosis, and a collection of well-selected experiments with carbohydrates, fats, proteids, and milk, together with a scheme for the qualitative analysis of commercial prepared foods.

The book contains the essentials of a course of laboratory work for the second year of study in most American Medical Colleges, at the same time it supplies physicians with a small handbook on chemical diagnosis as applied to the gastric contents, milk, fæces, and urine. The author acknowledges his indebtedness to Halliburton's "Essentials of Chemical Physiology," in preparing the course of experimental study of the proximate principle of foods.

The book can hardly be used without the "Text-book" containing descriptive chemistry; it opens with the experimental study of carbohydrates, fats, proteids, the albumenoids, milk, and saliva, the directions being concise, and assuming knowledge of elementary chemistry. More than half of the book is given to the study of urine, but the author does not undertake to teach physiology.

Tables of weights and measures, with an Index, close a compact, well-made handbook.

CORRESPONDENCE.

ANALYSIS OF THE ASH OF CARDAMOMS.

To the Editor of the Chemical News.

Sir,—In reference to Mr. H. B. Yardley's report on the ash of cardamoms, I was struck with the remark that "it was of a grey colour, probably due to a small quantity of carbon." And, further, on examining his analysis he made no mention of manganese. It is one of the characteristic features of zingiberaceous plants that most of them take manganese from the soil, and I am of opinion that, if Mr. Yardley repeats his work, he will find that the grey colour is due to manganese. Here is a copy of some analyses done by me not long ago on undoubted specimens of *Elettaria cardamomum*:—

Seeds (whole)	3·26	per cent of ash.
Seeds (crushed)	3·52	,, ,,
Pericarp of fruit	6·17	,, ,,
Pericarp of fruit	5·96	,, ,,
Entire fruit and seeds (six taken in each case) ..	3·8	,, ,,
	4·219	,, ,,

The ash in all cases contained an appreciable quantity of manganese. There are several reports on the ash of cardamoms, some giving as much as 15 per cent; but I am afraid that such an amount is far too high. There are so many varieties of cardamoms that it is just possible that there may be a wide variation in some species.—I am, &c.,

W. Watson Will.

Metropolitan College of Pharmacy,
162, Kennington Park Road, S.E.

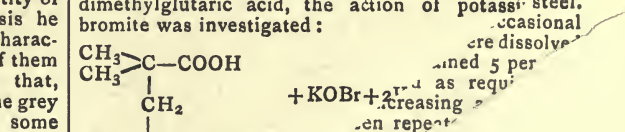
CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 11, March 13, 1899.

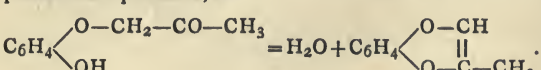
Double Cyanides.—M. Berthelot.—The double cyanides selected for experiment were combinations of potassium cyanide with those of zinc, mercury, and silver. The author classifies his research under three heads:—(1). The first part deals with the equilibrium between hydrocyanic acid and acids united with alkaline bases. Strong acids, *e.g.*, HCl and HNO_3, completely decomposed potassium cyanide, with evolution of heat. With weak acids, *e.g.*, C_6H_5OH, the base divided itself between the two acids, the hydrocyanic acid taking three-fifths of the base, for potassium phenolate is dissociated to a greater extent than the cyanide, though, at the same time, the heat of neutralisation of hydrocyanic acid is less than half that of phenol. In the case of weak, polybasic acids, such as H_2S, the results depended on the relative masses. Hydrocyanic acid gave no thermal reaction with alkaline sulphydrates. Boric and hydrocyanic acids shared the alkaline bases, the division depending on the relative proportions. (2). The second part deals with the heat of formation and constitution of double cyanides. On treating a solution of the double cyanide of silver and potassium with a strong acid silver cyanide was precipitated and the potassium cyanide decomposed. With weaker acids (acetic, boric, carbonic, &c.) the phenomena observed indicated the existence of a complex acid, argentohydrocyanic acid, analogous to ferrohydrocyanic acid. For example, carbonic acid produced no effect on the solution of the double cyanide, whilst arsenious and boric acids gave a slight crystalline deposit after some weeks. Acetic acid caused partial precipitation of silver cyanide. The results obtained on operating with the double cyanide of mercury and potassium are comparable with the above, showing that mercurohydrocyanic acid is less stable than argentohydrocyanic acid. In the case of zinc there were also indications of the existence of a zincohydrocyanic acid. The third part of the research, dealing with the action of hydrogen and alkaline sulphides on double cyanides, is not given.

Research on *αα*-Dimethylglutaric Acid.—E. Blaise.—In order to establish the constitution of dimethylglutaric acid, the action of potassium bromite was investigated:



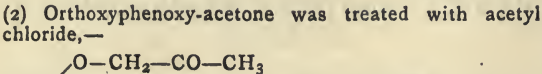
The esterification of the acid was also investigated. As a result, a great difference was found to exist between the two carboxyls.

Methylethylene Pyrocatechin.—Ch. Moureu.—This body is the second member of the series of compounds containing a benzene nucleus and a non-saturated dioxy-radicle. It has been prepared from orthoxyphenoxy-acetone by two methods:—(1) Orthoxyphenoxy-acetone was dehydrated by means of phosphoric anhydride in presence of quinoline,—



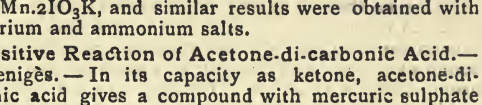
Methylethylene pyrocatechin.

(2) Orthoxyphenoxy-acetone was treated with acetyl chloride,—



Double Iodides of Manganese Dioxide.—A. Berg.—Few compounds are known in which manganese dioxide reacts as a basic oxide, and these are only stable in presence of an excess of acid. The author has discovered that iodic acid gives an iodate of manganese dioxide having properties analogous to those of the other salts of the same nature. Hydrated manganese dioxide was prepared by the action of potassium permanganate on a manganous salt, and this partially dissolved on boiling with a solution of iodic acid, giving a brown solution. It was not possible to isolate the iodate from the excess of iodic acid, on account of its instability; but in presence of certain metallic iodates more stable double iodates were produced. These compounds are insoluble in water, and not much attacked by it. The potassium salt had the formula $(IO_3)_4Mn.2IO_3K$, and similar results were obtained with the barium and ammonium salts.

Sensitive Reaction of Acetone-di-carbonic Acid.—G. Denigès.—In its capacity as ketone, acetone-di-carbonic acid gives a compound with mercuric sulphate corresponding with the formula—



This compound is insoluble in water, and forms a delicate test for traces of acetone-di-carbonic acid.

MISCELLANEOUS.

Australasian Association for the Advancement of Science.—We have received a copy of the Report of the Seventh Meeting of the Australasian Association for the Advancement of Science, held at Sydney in 1898. The Association is conducted on the same lines as the British Association, the matter is distributed over ten Sections, designated [illegible] A to J, the work in each Section commencing with an address by its President. In the Presidential Address [illegible] Liversidge, M.A., LL.D., F.R.S., the aims, objects, and [illegible] of the parent Institution, the British Association, are set forth in detail, and after a brief reference to the working of other similar institutions, a good *résumé* is given of the more recent advances and discoveries in science. From the number and scope of the papers presented in the various Sections, we conclude that the Australasian Society is in a very healthy condition and is doing really good work. Although mostly of local interest, the papers are none the less valuable; we particularly note the interesting papers in Section F (Ethnology and Anthropology). The volume, of 1161 pages, is well arranged and illustrated, and, considering the amount of matter included, we must congratulate the editors upon the promptness with which it has been issued.

MEETINGS FOR THE WEEK.

MONDAY, 10th.—Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "The Industrial Technical Treatment of Sherry and of British Colonial Wines," by Dr. J. T. W. Thudichum, F.R.C.P. (Lond.).
TUESDAY, 11th.—Royal Institution, 3. "Zebras and Zebra Hybrids," by Prof. J. Cossar Ewart, M.D., F.R.S.
WEDNESDAY, 12th.—Society of Arts, 8. "Telephones," by John Gavey, Assistant Engineer-in-Chief and Electrician, G.P.O.
THURSDAY, 13th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, M.A., LL.D., F.R.S.
FRIDAY, 14th.—Royal Institution, 9. "Earth Currents and Electric Traction," by Prof. A. W. Rücker, M.A., D.Sc., &c.
SATURDAY, 15th.—Royal Institution, 3. "Machiavelli," by Louis Dyer, M.A.

ROYAL INSTITUTION OF GREAT BRITAIN,
ALBEMARLE STREET, PICCADILLY, W.

Professor DEWAR, M.A., LL.D., F.R.S., M.R.I., Fullerian Professor of Chemistry, R.I., will, on THURSDAY next, APRIL 13TH, at Three o'clock, begin a Course of Three Lectures on—
"THE ATMOSPHERE."
Subscription to this Course, Half a Guinea.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E, M.S.C.I.,
Fellow of the Chartered Institute of Patent Agents,
NORFOLK HOUSE, NORFOLK STREET, LONDON, W.C.
"PATENTEE'S HANDBOOK" Post Free on application.

CHEMIST-ENGINEER.

Swiss, with highest references, graduated, knowing the English language, at present in an English Colony, with several years' experience in one of the largest Aniline Colour Works of the Continent, wants Situation in similar Works.—Address, "Z.L. 2111," care of Rudolf Mosse, Zürich, Switzerland.

Young Man desires to enter a good Firm of Analytical Chemists as Junior Assistant. Time given in lieu of wages.—Address. E. E., 5, Jerningham Road, New Cross, S.E.

Junior Assistant wanted in Laboratory, London.—Address, J. A., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, Post at home or abroad as Manager or Chemist; scientific training; good experience in the manufacture of B.O.V., R.O.V., Saltcake, Bleaching Powder, Caustic Soda, Nitric Acid, Dyers' Solutions, &c. Full particulars on application.—Address, M. C., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Wanted, an Analytical Chemist of exceptionally high and proved ability and accuracy, with good experience in testing Medicinal Chemicals, to take up the position of Chief Analyst at the Works of a leading London Firm of Manufacturing Chemists. A gentleman who has taken University Degrees preferred.—Address, stating age, qualifications, and experience, to "Analyst," care of Messrs. Markby, Stewart, and Co., Solicitors, 57, Coleman Street, London, E.C.

Wanted, at a Colonial Government Laboratory in the West Indies, a Chemist holding University Honours Degree to assist in Analysis and Research. Likely applicants will be furnished with full particulars.—Apply, stating age, whether married or single, and qualifications, to D. D., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

WELDON APPARATUS, Second-hand, wanted in thoroughly good working order and condition.—Address, Box 3756, Sell's Advertising Offices, Fleet Street, London, E.C.

FOR SALE.—One Assay and one Chemical Balance, both by Oertling; also two 15 inch diam. Assay Furnaces.—Apply, Messrs. Corbin & Greener, 85, Gresham Street, E.C.

THE CHEMICAL NEWS.

Vol. LXXIX., No. 2055.

THE ESTIMATION OF CARBON IN STEEL: APPARATUS AND MATERIALS.

The pneumatic stirring apparatus (Chemical News, lxxiv., 63), by means of which any number of samples of steel may be kept constantly agitated, has recently been modified in an important detail by H. Jervis (Chem. News, lxxix., 86). He proposes an additional piece of apparatus, one object of which is to prevent any irregularity in the working of the filter-pump causing the solution to be forced from one flask into another. The means proposed are admittedly inefficient when more than a certain number of flasks are attached to each other. I propose to show why the arrangement must fail ultimately, and to mention a precaution more than sufficient to cover the danger of as many attached flasks as the pump can agitate.

Mr. Jervis's apparatus, however finely it may be adjusted, can avail only when there is an actual backward pressure from the pump. The damage may be done before this point is reached.

Say two flasks are being agitated by a current of air moving in the arrowed direction, and that the foremost one is suddenly detached from the pump. The pressure in the flask A is that of the atmosphere, but the pressure in B is less, because the atmosphere must push back the column of liquid in the straight tube passing through B's perforated stopper before it can destroy the partial vacuum which existed before the pump was detached. But the straight tube passing through A's perforated stopper is in direct contact with the inside of B, and consequently the copper solution must rise in it when flask A is exposed to the normal pressure of the atmosphere.

A moment's reflection will show that the height to which the solution will rise in A's tube depends upon the depth B's corresponding tube dips below the surface, or, similarly, on the number of flasks following A whose tubes dip a certain distance below the surface of their solution. It is thus apparent that with no actual back pressure whatever, and notwithstanding the previously described arrangement, the solution of the first flask may pass into the second.

On the other hand, it should be noticed that the solution of flask B could not, under like circumstances, pass into a following one, C. The pressure in B's straight tube is the same as that of C's flask, and from previous considerations it is plain that the pressure in any flask (except A) is less than than that of any succeeding one, so that the solution of B could never pass into C, or C into D, and so on, unless the straight tubes were *very* short in comparison with the total column of liquid through which the air is drawn: such considerations have nothing to do with the present case.

Obviously the remedy lies in making it very difficult for the solution to pass from A into B, either by making A's straight tube very long or by using a heavy liquid in a flask permanently placed first in a series. The latter is the more convenient device, all that is needed being a small alteration of the Woulf bottle shown in the figured arrangement on page 86. Through each neck of the bottle a tube should pass. One, very narrow, dipping below a layer of mercury, is attached to the dissolving flask; the other, not reaching the surface of the mercury, is attached to the pump. The solution of A can now pass into B only after considerable mercury has been pushed over into A; but as the narrow tube can be made any length, the chances of this taking place may be made as remote as may be wished. It is, of course, just as necessary as ever to detach a long series the hindermost first.

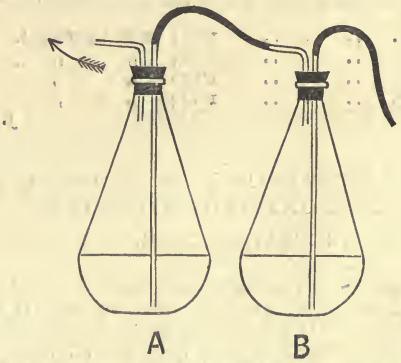
The dissolving of iron in copper solutions is usually expressed by the following equations:—

1. $Fe + CuCl_2 = Cu + FeCl_2$.
2. $Cu + CuCl_2 = Cu_2Cl_2$.

The ammonium, sodium, or potassium chloride is present chiefly for the purpose of retaining the cuprous chloride in solution.

The green copper solution begins to darken almost immediately it is brought in contact with the iron. This shows, if the operation is substantially represented by the above equations, that the second reaction follows close on the heels of the first. This must be so, because it is to the reaction between the copper and the copper ammonium chloride that the blackening is due, or, more strictly speaking, to the fact that this operation forms the cuprous in the presence of cupric chloride.

On dissolving metallic copper in an acid solution of copper ammonium chloride, the colour changes are:—Bright green, olive-green, light brown (black in the mass), dark brown, and then—if the copper is in excess—reddish brown, to a practically colourless solution of cuprous chloride. This solution, dropped into copper ammonium chloride, produces a black cloud, and we can thus exactly simulate the colour changes which attend the dissolving of an ordinary sample of steel. A mixture of no other of the compounds formed so satisfactorily explains the darkening of the solution.



The new compounds formed by dissolving a sample of steel are cuprous chloride and ferrous chloride. Both these bodies oxidise readily in the air, so that when the solutions are pneumatically agitated they become partially re-oxidised. By continuing to pass the air the oxidation is nearly completed, and the solution regains its original green colour.

The question very naturally arises as to whether such a solution can be advantageously re-used, and, if so, how often?

Three hundred c.c. of a saturated solution of copper ammonium chloride was agitated with 5 grms. of steel. Keeping the filtrates at about 300 c.c. by occasional evaporation, successive lots of 5 grms. each were dissolved and filtered. The original solution contained 5 per cent strong HCl, and more acid was added as required, in order to form the chloride of the increasing amounts of iron. After this operation had been repeated four or five times, there was a decided decrease of the rate at which the solution could be filtered. The filtration of the seventh sample was decidedly slow, and that of the eighth impossible without previous dilution. Before the eighth sample was dissolved, crystals separated; not crystals of an iron salt, as I had hoped, but crystals of copper salt. Had the iron crystallised out, a theoretically unending use of the same solution would have been possible.

The carbonaceous residue of the first six samples, with

no other precautions than attach to every-day technical estimations, were combusted. The results were:—

I.	.. .. ..	1·21 carbon per cent.	
II.	.. .. ..	1·19	,, ,,
III.	.. .. ..	1·18	,, ,,
IV.	.. .. ..	1·20	,, ,,
V.	.. .. ..	1·20	,, ,,
VI.	.. .. ..	1·19	,, ,,

In another case the samples were successively added without filtering off the the separate carbonaceous residues. Here, as before, the sixth, seventh, and eighth samples were dissolved much slower than the first three or four samples. The combustion of the total residue of the 40 grms. of steel used gave 1·16 per cent carbon.

From these experiments it is apparent that, after dissolving one sample, the copper ammonium chloride need not be regarded as useless.* It may be used three or four times where the convenient practice is adopted of allowing the sample to be dissolved during the night.

Neutral copper solutions cannot be so conveniently used with the pneumatic stirrer, because the iron after oxidation is thrown out and messes the flask and tubes. If, however, the sample be dissolved by shaking in a stoppered flask, the solution may be filtered without any appreciable amount of iron being thrown out. The filtrate can then be oxidised by the air current, the iron oxide allowed to settle, and the clear green solution re-used. Theoretically there is no limit to the number of times a solution may be used in this way. The following are the results of four carefully combusted residues obtained by the successive use of the same solution:—

I.	.. .. ..	1·184 carbon per cent.	
II.	.. .. ..	1·184	,, ,,
III.	.. .. ..	1·178	,, ,,
IV.	.. .. ..	1·184	,, ,,

J. T.

THE PRECIPITATION OF CADMIUM BY SULPHURETTED HYDROGEN.

By ROBERT MELDRUM, F.C.S.

In the qualitative examination of solutions for cadmium, it is usual to acidify with HCl, heat, and pass H_2S gas through same. HCl is not the most reliable agent for this purpose, as will be seen from the following table. Column I. = grms. $CdSO_4.xH_2O$ in 10 c.c. of H_2O precipitated in cold by H_2S gas. Columns II. and III. = c.c. of strong HCl required to dissolve precipitate to a colourless solution.

I.	II. At 10° C.	III. At 100° C.
0·050	3·0	1·0
0·045	4·0	0·9
0·040	3·5	0·8
0·035	3·5	0·9
0·030	3·0	0·8
0·025	3·0	0·8
0·020	2·5	0·8
0·015	2·5	0·6
0·010	2·0	0·5
0·005	1·5	0·4
0·0025	1·5	0·3

Several cases of failure to discover cadmium when present in appreciable quantity have of late come under my notice, and I have no doubt that this is due to excess of HCl being present. Acetic and sulphuric acids have little or no solvent action on the precipitated sulphide, even when present in excessive proportion. Cases will occur where the solution contains excess of chlorides of the metals decomposable by H_2S with liberation of HCl, and it is especially here where small quantities are liable to escape detection.

Neutral solutions containing from 0·025 to 0·05 grm. $CdSO_4.xH_2O$ or more per 10 c.c., when precipitated in the cold by H_2S gas, give a canary-yellow curdy precipitate, which settles in a few minutes, leaving a dense opaque yellow solution above. Heated to boiling, the precipitate changes to orange-yellow, settling rapidly and leaving the liquid clear with a slight yellow tinge. As the solution cools, the orange-coloured precipitate becomes—to a slight extent—paler, but does not regain its former colour. If the hot solution be agitated while cooling, and when thoroughly cold, the precipitate settles slowly, leaving an opaque solution above. From these properties alone, it is possible to distinguish the yellow precipitate of cadmium sulphide from all other precipitates, and seem to me to be very characteristic.

In solutions containing from 0·02 to 0·005 grm. of the cadmium salt per 10 c.c. a precipitate falls in a few minutes, leaving a yellowish opalescent solution above. All change to dark yellow on boiling, but do not clear rapidly, remaining somewhat milky.

In solutions containing from 0·0025 to 0·002 grm. of cadmium salt per 10 c.c. a strong yellow opalescent solution results from which no precipitate settles out in thirty minutes. On boiling, a small precipitate settles out from each, leaving the solution faintly yellow.

0·00175 grm. in 10 c.c. gives opalescent solution of a strong yellow colour, yielding no precipitate on standing for one hour or on boiling.

0·00125 to 0·0015 grm. in 10 c.c.: faintly opalescent solution, from which no precipitate settles out in one hour. 0·001 to 0·00075: very distinctly yellow solution. 0·0005: in 2-inch column distinctly yellow. 0·000125: no colour in 2-inch column.

All the above are only apparently yellow solutions, as on standing for twenty-four hours, the sulphide—which appears to exist in the colloidal state—undergoes a change to the amorphous condition, and falls to the bottom as a yellow precipitate, leaving the solution of a faintly yellow tint. In all precipitations of cadmium in neutral solutions by H_2S, the greater part of the sulphide is in the amorphous state, a very small part in the colloidal state, and—as we shall presently see—a still smaller proportion in the soluble state. Solutions of cadmium containing more than 0·0175 per cent of the salt, when precipitated by H_2S gas, yield a filtrate almost free from colour in 2-inch columns; whereas, should the Cd be present in lesser quantity than this, the filtrate is always highly coloured. Thus:—

0·025	per cent.	No colour in 2-inch column of filtrate.
0·015	,,	Faint trace of colour in 2-inch column of filtrate.
0·0125	,,	Colour of filtrate very distinct.
0·010	,,	Filtrate highly coloured.
0·0075	,,	,, ,,
0·005	,,	,, ,,

Solutions containing from 0·0175 to 0·015 per cent of salt, when re-filtered several times through the same paper, the filtrate is latterly as colourless as water. Weaker precipitated solutions than these may be re-filtered over and over again without any appreciable decrease in colour, thus indicating that the cadmium in these cases exists in the soluble condition. If these filtered solutions are allowed to stand over twenty-four hours, a small precipitate always settles out, the solution still retaining a faint yellow colour.

To account for strong precipitated solutions of cadmium yielding an almost colourless filtrate, and weaker solutions a coloured one, two explanations present themselves.

* I know that in some laboratories the practice of a system of fractional crystallisation enables the bulk of the iron to be concentrated in a volume of mother-liquor some five or six times less than the original volume of the filtrates, and provides also crops of crystals of more or less pure copper ammonium chloride, which may be used for dissolving steels.

(1) In the case of strong solutions, the large curdy precipitate entangles the colloidal and soluble sulphides and carry them down, in the same way that any other bulky precipitate would carry down other gelatinous and soluble matter when present in small proportion. (2) That the large precipitate forms a film on the paper preventing the passage of both the soluble and colloidal forms.

I find that cadmium under a great many circumstances may be accurately estimated by a colorimetric method based upon the above properties when the amount of Cd present does not exceed 0·02 per cent $CdSO_4.xH_2O$.

THE DETERMINATION OF ARSENIC IN GLYCERIN.

By A. C. LANGMUIR.

The presence of arsenic in glycerin is probably by this time well known to chemists. Several have described its detection qualitatively. Barton (*Journ. Amer. Chem. Soc.*, xvii., 883), however, was the first to estimate it quantitatively. Barton's method, which was applied on C.P. glycerins only, consists in the charring of 5 grms. of the glycerin with sulphuric and nitric acids, the production of a mirror in the Marsh apparatus, and the comparison of the mirror so obtained with a standard mirror according to Sanger's method (*Proc. Am. Acad. Sci.*, 1891, xxvi., 24).

As it is impossible to draw an accurate comparison if the mirrors weigh over 0·06 milligrm., a suitable aliquot part of the solution must be taken, in order to obtain a mirror weighing less than this amount. This requires some experimenting on the part of the analyst, which becomes very tedious if the glycerin be high in arsenic.

These considerations led the author to abandon the method and adopt a modification of Polenske's process (*Chem. Centrbl.*, 1889, lx., [2], lviii.), suitable to the case at hand. The method as described by Polenske is accurate with quantities of arsenic up to 4 to 5 milligrms. As in glycerin analysis the amount of arsenic in the portion taken rarely exceeds 1 milligrm., the apparatus may be materially simplified.

For analysis we take 15 to 20 grms. of a crude soap lye glycerin and 25 to 30 grms. of a saponification or C. P. glycerin. With dilute glycerins an amount is taken which would yield the requisite weight upon evaporation. The weighed sample is made up to 100 c.c. with hot water and rinsed into a capacious casserole, containing a mixture of 200 c.c. of concentrated nitric acid, and 12 c.c. concentrated sulphuric acid. Cover and heat gently in the hood until the action starts. Remove the flame and wait until the violence of the reaction is over, then boil down slowly over a low flame until dense fumes of sulphuric acid appear. Raise the heat at the end to expel the last traces of nitric acid. If the concentration has been a slow one (four to five hours) the organic matter will generally be entirely oxidised. If the acid turns brown, however, from the charring of organic matter, it is well to boil for some time longer to complete the oxidation. There is no danger of losing any arsenic by this treatment. Cool and dilute to 50 c.c.

About 40 grms. of coarsely granulated zinc are placed in the generating flask of the Marsh apparatus. A 75 to 100 c.c. stop-cock funnel pierces the stopper. The escaping gas is passed through a wash-bottle containing a 5 per cent lead nitrate solution to remove any hydrogen sulphide, and is dried by passing through a calcium chloride tube. A tube of hard glass about 10 inches long and with an inside diameter of 10 to 12 m.m., is heated near one end and drawn out at that point to a tube with a diameter of 1 to 1½ m.m. This section serves to catch the metallic arsenic deposited. Of the large sections the longer is heated by two Bunsen burners. To prevent sagging it is well to protect this part of the tube with a roll of copper gauze wrapped around it. The shorter section at the end of the tube holds a slip of filter-paper moistened with a saturated solution of mercuric chloride. This serves to detect the presence of any hydrogen arsenide which might pass the burners undecomposed.

After making connections 10 c.c. of 20 per cent sulphuric acid is run into the flask. When the air has been entirely displaced rinse the solution to be tested into the stop-cock funnel, light the burners and run the solution, drop by drop, on the size at such a rate that not more than two bubbles a second pass the lead nitrate wash-bottle.

If the mercuric chloride paper should at any time show a yellowish tint the solution should be run in more slowly. If the size of the mirror shows that a considerable amount of arsenic is present, it is well to add, at the end, a little stannous chloride dissolved in hydrochloric acid. In any case add a few cubic centimetres of dilute acid after the entire solution has been run in to expel hydrogen arsenide remaining in the flask.

The section carrying the mirror is separated by a file and carefully weighed on an assay gold balance within 0·01 milligrm. This can be readily done, as the weight of the tube seldom exceeds 300 milligrms. The arsenic is dissolved by dipping the tube into hot dilute nitric acid, and after washing and drying the weight is taken again, the difference being the weight of the arsenic forming the mirror. The zinc and acids used should not form a perceptible mirror after running the apparatus three quarters of an hour. The following results were obtained:—

Arsenic taken. Milligrms.	Arsenic found. Milligrms.
0·20	0·17
0·50	0·45
0·75	0·68

Several C. P. glycerins were found to be free from arsenic. Arsenic was found in a majority of saponification glycerins. These averaged about 0·00018 to 0·00030 per cent. A number of crude soap-lye glycerins gave percentages lying between 0·00064 and 0·01.

A very fair idea of the arsenic contents may be gained by Gutzeit's test, using mercuric chloride instead of silver nitrate. Two c.c. of glycerin are run into a five-inch test-tube and diluted with 4 c.c. of water; a piece of granulated zinc is added and sufficient hydrochloric acid to just start the reaction. The tube is then quickly closed by a cork whose lower end is covered with a 7 c.m. filter-paper. The paper is wrapped around the cork so that it rests smoothly against the lower end. This part is moistened with two drops of a saturated solution of mercuric chloride. The hydrogen escapes through the creases between the paper and the tube. The evolution of hydrogen should be fairly brisk but not too violent.

After standing ten minutes the cork and paper are removed. The latter is spread out and examined. A yellow stain in the shape of a circle with a diameter equal to the end of the cork is formed if arsenic were present. With very impure glycerins the colour is brown. The papers carrying the stains may be marked and kept as records for future comparisons. The colour is fairly permanent. By comparing the yellow stain produced by the glycerin under examination with a series of standards prepared by running the same test on portions of a solution of arsenic (1 milligrm. in 100 c.c.). the per cent of arsenic can be gauged quite accurately after a little practice. The colour is quite distinct with 0·01 milligrm. of arsenic and is still perceptible with 0·0025 milligrm. If the latter amount were present in 2 c.c. glycerin (sp. gr. 1·26) the per cent of arsenic present would be 0·00010, which would be about the limit of delicacy by this test.

Gutzeit's test using silver nitrate was found to be very unsatisfactory. It is very difficult to form any idea as to the amount of arsenic present from the intensity of the colour in this case. The silver nitrate is also so easily affected by impurities in the zinc and acid other than

arsenic that any conclusion as to the presence of the latter should be drawn with great caution.

In view of the rapidity, delicacy, and accuracy of Gutzeit's test, using mercuric chloride, it is difficult to understand why the more laborious Marsh test should still hold its own as a qualitative test for arsenic.—*Journal of the American Chemical Society*, xxi., No. 2.

ON THE ACTION OF ALUMINIUM AS A REDUCING AGENT.

By L. FRANCK.

The Action of Aluminium on Compounds of Phosphorus.—The vapour of phosphorus when caused to impinge on powdered aluminium, heated to a dull red in a current of hydrogen, combines with this metal with incandescence. An agglomerated mass is formed, of a blackish-grey colour, which decomposes on contact with moist air, giving PH_3 and leaving a greyish-white residue. Water also decomposes this body, giving a hydrate of alumina and a brown residue. It is again decomposed by acids and alkalis, which dissolve it almost completely, giving off phosphoretted hydrogen. Heated in air this compound remains unchanged.

At more or less elevated temperatures all the derivatives of phosphoric acid (meta-, ortho-, and pyro-salts) are decomposed by aluminium. But it is the metaphosphates which undergo the most complete transformation. The reaction is represented by the equation—

$$6NaPO_3+15Al=6NaAlO_2+2Al_2O_3+Al_5P_3+P_3.$$

By adding silica the reaction becomes—

$$6NaPO_3+10Al+3SiO_2=3Na_2SiO_3+5Al_2O_3+3P_2.$$

The salts of calcium or magnesium are as efficacious as those of sodium, but commercial superphosphates cannot be made to serve for the preparation of phosphorus by this method. On the contrary, we obtain excellent results by using the ash of bones decomposed by hydrochloric instead of sulphuric acid.

In this manner phosphorus can be prepared with almost quantitative results, at relatively low temperatures.

The Action of Aluminium on Carbon Compounds.

1. *On Carbonic Acid.*—When dry carbonic acid is passed over powdered aluminium heated to redness, the temperature rises rapidly, owing to the reaction which is developed. On allowing the product of this reaction to cool in carbonic acid, we notice that alumina and amorphous carbon are formed; but if we treat this with hydrochloric acid, a gas with a disagreeable odour is given off, indicating that carbide of aluminium has been formed. The reaction corresponds exactly to the equation $3CO_2+4Al=2Al_2O_3+3C$.

2. *On Carbonic Oxide.*—We obtain the same results as in the preceding case. The reaction is as follows:—$3CO+2Al=Al_2O_3+3C$. As in the case of carbonic acid, a little carbide of aluminium is formed.

3. *On the Carbonates.*—A mixture of an alkaline carbonate with metallic aluminium, prepared in proportions corresponding to the equation—

$$Na_2CO_3+2Al=Al_2O_3+C+Na,$$

and heated to redness, becomes incandescent. The products of the reaction are metallic sodium and amorphous carbon.

The author has succeeded in reducing lithium, sodium, potassium, calcium, barium, and strontium in this manner.

4. *On Carbon.*—The author confirms the opinion of MM. Guntz and Masson, according to which the presence of iodide or chloride of aluminium favours the formation of the carbide when aluminium is heated in carbonic acid or carbonic oxide. Powdered aluminium heated with lampblack appears at first to have undergone no change, but under the action of water it gives off a large quantity of hydrocarbon gas. It is, however, impossible to separate the excess of lampblack. We can obtain a large proportion of carbide of aluminium by the direct combination of these two elements, but pure carbide cannot be prepared except by the aid of the electric furnace.

Action of Aluminium on the Oxides.—The mixture of oxide of copper and aluminium in proportions calculated for the theoretical reduction detonates violently when heated to redness. With a large excess of aluminium a bronze is obtained. The reaction is identical with oxide of silver. Oxide of glucinum is also reduced, but only with incandescence. Lime may also be partially reduced by aluminium, and this process would enable us to prepare alloys of calcium, but this is doubtful. The same applies, but in different degrees, to barium and strontium. Finally, aluminium reduces, more or less easily, the oxides of zinc, cadmium, mercury, lead, boron, silicon, phosphorus, arsenic, iron, manganese, cobalt, nickel, and molybdenum.

These reactions have long been known, and Keller has generalised them in a very complete work ("Contributions to the Study of Reducing Agents," *Moniteur Scientifique*, March, 1896, p. 190).

Action of Aluminium on Sulphates and Chlorides.—The mixture of aluminium with sulphate of baryta (or any other sulphate) detonates when heated. Among the products of the reaction we find finely divided sulphur and sulphides. All the chlorides are reduced by aluminium.

Action of Aluminium on Peroxide of Sodium.—The mixture of these two bodies detonates on heating. By moistening with water it is spontaneously inflammable.—*Chemiker Zeitung*, 1898, p. 236.

ON A CRYSTALLINE BASIC CHLORATE OF COPPER.

By L. BOURGEOIS.

It is well known that the careful decomposition of the neutral nitrate of copper, by the action of heat, readily gives a crystallised basic nitrate, which I have shown (*Comptes Rendus*, 1890, cx., 541) to be identical with gerhardtite, a mineral found in the United States by Messrs. Brush, Penfield, and Wells (*Amer. Journ. Sci.*, [3], 1885, xxx., 59). This same basic nitrate,—

$$4CuO.N_2O_5+3H_2O,$$

occurs either in the orthorhombic form of gerhardtite or in the state of the dimorphous clinorhombic variety, according to circumstances; in every case the neutral nitrate loses nitric acid, as has been shown by several chemists, notably G. Rousseau (*Comptes Rendus*, 1890, cxi., 38), L. Michel (*Bull. Soc. Min.*, 1890, xiii., 139), Atanasesco (*Bull. Soc. Chim.*, 1894, xi., 1112), and myself (*loc. cit.*).

Following quite another line of thought, the works of Mallard (*Bull. Soc. Min.*, 1894, vii., 349—401) have called attention to the isomorphism existing between the nitrates and the chlorates,—a very important fact from the chemical point of view, since it tends to show that the chlorine in the chloric acid should be triatomic or pentatomic. Basing our ideas on these relationships, we may well ask if the neutral chlorate of copper, a salt of which the chemical composition and the properties altogether agree remarkably with those of the nitrate, would not also give a crystallised sub-salt corresponding to gerhardtite.

The existence of a basic chlorate of copper was in 1843 described by Al. Waechter (*Journ. f. Prakt. Chem.*, 1843, xxx., 321; *Journ. de Pharm. et de Chim.*, [3], 1844, v., 360) as resulting from the decomposition of chlorate of copper by the action of a moderate heat; and from the complete

work of this chemist on the metallic chlorates we gather that, alone among these, chlorate of copper undergoes a decomposition comparable to that of the nitrate. Waechter describes the basic chlorate as being a green body, insoluble in water, very soluble in acids; but he gives no analysis, and does not mention whether there are any indications of crystallisation.

The communication I have the honour of presenting to the Society has for its object to decide whether the green salt of Waechter corresponds chemically and crystallographically with gerhardtite, and to see whether it is as easily formed as this body under practically similar circumstances.

If, for example, we heat in a flask on the sand-bath crystals of chlorate of copper, $(ClO_3)_2Cu+6H_2O$, we observe that they melt at about 65° in their water of crystallisation, giving a blue liquid of a syrupy consistence. The decomposition of the salt commences, though very slowly, at about 100°; towards 110° to 120° it is rapid, without being violent. We then notice that the liquid takes a cloudy deep-blue tint rather inclined to green, and gives off small bubbles of gas (peroxide of chlorine, chlorine, and oxygen), while at the same time continuous decrepitation is heard.

The greater part of these phenomena accompanying the decomposition of the chlorate have been described by Waechter. Soon the basic salt is deposited, and a crystalline appearance is already manifest to the naked eye. When the mass has become sufficiently thick owing to the deposition of crystals, the operation is stopped; after cooling we wash with cold water, which removes the undecomposed neutral chlorate; the crystals are thrown on a filter, washed, and dried.

If, in the same manner, we had carefully heated crystals of nitrate of copper on the sand-bath, but to a slightly higher temperature, we should, as is well known, have obtained gerhardtite. The formation of this body is easily explained; it should be remarked that the nitrate of copper decomposes very distinctly into gerhardtite and nitric acid, $NO_3H+3/2H_2O$; the vapours of this latter condense on the cooler parts of the vessel, fall back on the small vessels which have just been formed, partially dissolving them, and this reversible reciprocal reaction going on continuously enables the crystals to increase in size. It is less easy to account for the production of the crystals of subchlorate of copper, inasmuch as chloric acid is not volatile without decomposition, and the salt is formed during the course of a reaction which is not only not reversible, but even appears to be slightly explosive.

On the other hand, we have proved that the subchlorate of copper dissolves with heat into a very concentrated liquid of neutral chlorate, and that this solubility increases with the temperature and the concentration. Thus we find realised, from the continuous movements which accompany the decomposition of the chlorate, conditions enabling the crystallisation of the basic salt to take place. When we take up the mass with water after cooling, we always get, besides the already formed crystals, a very slight bluish green cloudiness, due to a deposit entirely formed of micro-crystalline basic chlorate. Pressure also varies the speed of decomposition of the chlorate of copper; if we operate *in vacuo* the reaction becomes violent, and only gives an amorphous product (it is the same with the nitrate); in a sealed tube it appears to be retarded, but nevertheless gives off chlorine and oxygen; the dimensions of the crystals, however, do not increase as I had hoped.

The same salt is also formed when we heat a solution of chlorate of copper with fragments of marble, or again with urea, to about 130° in a sealed tube, but the crystals obtained are less voluminous than those furnished by the first process.

Basic chlorate of copper exists in the form of small tablets of a very beautiful green colour, often reaching several tenths of a millimetre, and sometimes even 1 or 2 m.m. in diameter; their density is 3·55. At first sight they resemble gerhardtite, only the tablets of this latter are more jagged and irregular. Further on we shall treat of their crystallographic and optical poroperties. The substance is insoluble in water, but easily soluble in even the weakest and most dilute acids; the well-known reactions of the chlorate can be easily recognised, and it can be easily shown that there is no chlorine present in the state of chloride. On calcination it becomes black, gives off water, chlorine, and oxygen, and leaves a residue of cupric oxide, which, contrary to Waechter's opinion, is not pure, but still retains chlorine in the form of cupric oxychloride or of cuprous chloride.

The salt has been analysed by dissolving it in the cold in water, to which just sufficient nitric acid has been added; the dilute liquid is then saturated with a solution of carbonate of sodium, which is added until all the copper is precipitated. We then boil the liquid for some time, so as to convert the basic carbonate of copper into black oxide, which is collected on a filter and weighed. The filtrate is evaporated to dryness, leaving a residue of chlorate of sodium with a little nitrate and carbonate. This is gradually calcined until it reaches a dull red heat; all the chlorate is then converted into chloride. Take up with water, acidulate with nitric acid, and estimate the chlorine with nitrate of silver. Thus for 100 parts of material we get the following results, which lead to the formula $4CuO.Cl_2O_5+3H_2O$ or $(ClO_3)_2Cu+3Cu(OH)_2$, corresponding to that of gerhardtite:—

	I.	II.	Calculated.
Cupric oxide	60·2	60·0	60·8
Chloric anhydride (theoretical)	—	28·4	28·8

It is now time to try and discover if the chemical analogy shown to exist between our product and gerhardtite exists also crystallographically. A superficial examination would lead us to say Yes; the crystals of the basic chlorate form, in fact, tablets with an irregular hexagonal contour, which might be derived from an orthorhombic prism with the base p predominant, and with facets with zones ph' and pm. The birefrangibility is strong, the extinction of parallel polarised light takes place along the large facets h', the angle mm measured under the microscope as a plane angle is about 94° 30'; now the value of the angle mm of gerhardtite is 94° 50'; there should therefore be isomorphism with this latter. A closer study, however, particularly with regard to its properties with convergent polarised light, leads us to altogether different conclusions. The direction of elongation is positive, and the plane of the optical axes is parallel to the direction of elongation of the faces (which we will call ph'). The flattened face p is very little out of being normal to the obtuse bisector n_p, and makes a small angle with the mean axis of optical elasticity n_m; the acute bisector n_g is contained in the plane of the face parallel to its elongation. These facts can be explained by comparing our basic chlorate not with gerhardtite, but with the dimorphous nitrate of this latter, obtained artificially by Messrs. Penfield and Wells, also by M. Rousseau. We get, in fact, in this last product, which is clinorhombic, for the angle mm measured on the base p, the value 94° 50', happily equal to the di-hedral angle mm in the dimorphous species, and very close to that of the plane angle found in these crystals. On the other hand, they have facets of which the angles with the principal face, p, could be measured with the goniometer on the largest samples, although the images were rather defective: these angles are of 114° 22' and 107° 5'. Now in the dimorphous specimens of gerhardtite we calculate, from the data given by Messrs. Penfield and Wells, that, if the facets $o\frac{1}{2}$ and $b\frac{1}{2}$ existed, we should have $po\frac{1}{2}=150°50'$, and $pb\frac{1}{2}=106°3'$ These considerations force us to admit that our crystals correspond to the dimorphous clinorhombic variety of gerhardtite, and not to this latter body itself, and that they possess the faces p, $o\frac{1}{2}$, and $b\frac{1}{2}$.

The neutral bromate of copper (prepared by the double

decomposition between bromate of barium and sulphate of copper) heated gradually at the ordinary pressure, as was done with the chlorates, decomposes more rapidly, giving off oxygen and bromine vapour; the phenomenon goes on, the same as with the chlorate or the nitrate, when heated *in vacuo*. We obtain basic bromate in the form of a very fine greenish blue powder, in which no crystalline form can be recognised even with the highest magnifying powers.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 23.

A REVISION OF THE ATOMIC WEIGHT OF NICKEL.*

Second Paper.—The Determination of the Nickel in Nickelous Bromide.

By THEODORE WILLIAM RICHARDS
and
ALLERTON SEWARD CUSHMAN.

(Continued from p. 166).

The question now arises, whence came this nickel? Was it occluded as nickelous bromide in the interior of crystals of sodic bromide, and thus protected from reduction, or was it dissolved as hydroxide from the spongy metal? The large quantity of nickel present seemed to overthrow the former alternative, but the possibility of the latter is emphatically denied by Winkler (*Zeit. Anorg. Chem.*, iv., 12), and rejected after some hesitation by Krüss (*Zeit. Anorg. Chem.*, ii., 238). Since the equivalent of nickelous bromide is very near that of sodic bromide (109·3 : 103), and the impurity was calculated from the amount of bromine present, the point has no important bearing on the immediate problem; but nevertheless it is always interesting to settle a mooted question of this sort.

Winkler's experiments were made with coherent nickel coated on the inside of a platinum dish, while Krüss's experiments were made with spongy metal in porcelain vessels. The former found no trace of any substance in the water in which his nickel had been digested, while the latter found a large residue (most of which must have come from the porcelain), and hastily ascribed this residue to the presence of an unknown element. It is not at all impossible that, in spite of the well-known permanence of the smooth bright surface of a nickel-plated object, the spongy metal reduced by hydrogen might be easily oxidised and dissolved.† The difference in this respect between polished iron and the same metal reduced by hydrogen is well known. Hence Winkler's experiments prove nothing with regard to the behaviour of finely divided nickel. The position of nickel on the positive side of hydrogen in the electro-chemical series leads one to expect that it must behave as zinc and iron do, although to a less degree. (See a paper entitled "Autoxydation," by R. Ihle, *Zeit. Phys. Chem.*, xxii., 114).

In order to decide the matter so far as the present work is concerned, we sought to determine experimentally, first, if the purest water is capable of acting on the purest nickel, and secondly, if the hydroxide thus formed is slightly soluble in water. To settle the first point, some very pure reduced nickel was thoroughly washed with water, and then digested at 20° for some time with repeated portions of water just purified. In every case nickel could be found in the filtrate, both by means of potassic thiocarbonate and by evaporation to dryness. Many repetitions of the experiment with new samples of metal brought always the same result. It is quite possible that galvanic action hastened this oxidation, for of course the nickel was contained in a platinum dish. Since Winkler's dish was evenly coated, the water probably did not touch the platinum in his case, and hence this possible cause of acceleration was absent; but the difference between the smooth surface and the finely divided surface alone is amply sufficient to explain the difference in the speed of the reaction.

It will be remembered that Krüss, in one of his experiments, digested a mass of nickel for a year on the steam bath with water, and obtained a white residue which was the chief basis of his alleged discovery. Our work shows that this residue must have contained not only dissolved porcelain, but also enough nickel to yield the black sulphide, the pale green colour, and the electrolysed metal which led Krüss so far astray.

It is clear that, since no acid was present in the water, *the nickel must have been dissolved in the form of hydroxide.* In none of our experiments with the purest metal did the solution give an alkaline reaction with phenolphthalein; hence hydroxyl ions must be absent, and the hydroxide must be dissolved in a colloidal form. The alkaline reaction sometimes observed by Krüss and Winkler must have been due to impurities, as Winkler pertinently suggests. Traces of alkali would surely be found in nickel oxide precipitated in glass vessels, even when mercuric oxide was used as the precipitant.

Nickelous hydroxide, precipitated by alkali and thoroughly washed, possesses at least as great solubility as the hydroxide which is formed by the slow oxidation of nickel. Upon suitable electrolysis, 15 c.c. of such a *cold* solution yielded 0·00062 grm. of nickel, while another similar portion yielded 0·00057 grm., or about 0·04 grm. per litre. Since the solubility is a colloidal one, its limit is indeterminate; hence no elaborate attempt was made to discover its exact amount. It is well known that the presence of other salts in the solution diminish this kind of solubility, but the small amount of sodic bromide present in this case was insufficient to produce any considerable effect. Undoubtedly the fact that the solubility is colloidal and uncertain is responsible for the conflicting statements of the various authorities and handbooks.

(Finkener, "Handbuch der Anal. Chem. von Rose, 6te Auflage von Finkener," ii., 136; Busse, *Zeit. Anal. Chem.*, xvii., 60; Fresenius, "Quant. Anal.," 1877-1887, ii., 393, 823; Roscoe and Schorlemmer, "A Treatise on Chemistry," vol. ii., Part 2, p. 149; Winkler, *loc. cit.*; Krüss, *loc. cit.*; &c. Temperature is a circumstance which produces great effect on this kind of solubility, heat being apt to coagulate the dissolved material).

This solubility of nickelous hydrate is the circumstance which obliged us to determine the residue of sodic bromide through argentic bromide, instead of simply by evaporating the wash-waters poured off from the nickel and weighing the residue. This necessity is made clear by the following table:—

No. of Anal.	Weight of nickel.	Weight of residue extracted by water and dried at 105° C.	Weight of AgBr.	Weight of NaBr calculated from AgBr.	Weight unaccounted for.
	Grm.	Grm.	Grm.	Grm.	Grm.
6.	0·805	0·00330	0·00410	0·00225	0·00105
7.	1·488	0·00895	0·01398	0·00767	0·00128
8.	0·607	0·00400	0·00568	0·00311	0·00089

In order to prove that this large percentage of unexplained residue consisted chiefly of nickelous hydrate, two more determinations were made with new material. Since enough data for the atomic weight had been obtained, and time pressed, the bromide of nickel was not weighed in the first place. In these analyses the *nickel* dissolved as hydroxide was also weighed.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No 13, February, 1899.

† It is a peculiar household fact that cold water faucets plated with nickel are usually less brilliant than their hot water comrades; this difference may well be ascribed to the slow action of condensed water, even upon polished nickel. The greater tendency to rust shown by cobalt may well be due to the fact that in its case the hydroxide is converted into a higher state of oxidation immediately upon being dissolved, thus giving opportunity for the solution and hence for the formation of more hydroxide. In the case of nickel the thin permanent film of $Ni(OH)_2$ probably protects the metal, although its solubility may be no less than that of $CO(OH)_2$.

	Grm.	Grm.
Weight of residue obtained, dried at 105°	0·00925	0·00480
Argentic bromide found	0·01405	0·00630
Nickel deposited electrolytically ..	0·00092	0·00084
Sodic bromide calculated	0·00770	0·00345
Nickelous hydroxide calculated ..	0·00146	0·00133
Total calculated weight of residue..	0·00916	0·00478
Weight unaccounted for	0·00009	0·00002

Besides this quantitative proof that the residue consisted of nothing but sodic bromide and nickelous hydrate, many qualitative analyses had shown the absence of lime, alumina, silica, and even potash, from the solution poured off from the reduced nickel. Traces of sulphuric acid were found, as has been said, only in the first specimens.

In the light of all these results, no doubt seemed to remain as to the proper mode of correcting the direct gravimetric results of the reduction. Obviously the weight of the sodic bromide must be subtracted from the weights of both the nickelous bromide and the metal formed from it by the action of the hydrogen; for the salt existed in each. On the other hand, the nickelous hydroxide was simply to be neglected; for this substance was formed after the last weighing had been finished. The temperature used for the reduction was so low that no sodic bromide was vaporised; at least none could be found in the cooler parts of the reduction tube.

Analyses 5 and 6 were made with nickelous bromide of the grade of purity represented by the numeral II. in the former paper, while all the others were made with that labelled III., which had been made through the carbonic oxide process. The headings of the various columns will show with sufficient clearness the meanings of the figures given in the accompanying table.

The Atomic Weight of Nickel.

FOURTH SERIES.—O=16. Ratio = $NiBr_2$: Ni.

No. of analysis.	Sample.	Weight of nickel bromide in vacuum.	Weight of nickel in vacuum.	Weight of sodium bromide to subtract.*	Weight of nickel bromide corrected.	Weight of nickel corrected.	Atomic weight of nickel.
1.	III.	2·83610	0·76366	0·00285	2·83325	0·76081	58·705
2.	III.	3·21908	0·86641	0·00283	3·21625	0·86358	58·696
3.	III.	2·31578	0·62431	0·00337	2·31241	0·62094	58·703
4.	III.	2·88330	0·77707	0·00377	2·87953	0·77330	58·710
5.	II.	2·29843	0·61872	0·00193	2·29650	0·61679	58·719
6.	II.	2·99118	0·80497	0·00225	2·98893	0·80272	58·714
7.	III.	5·52058	1·48823	0·00767	5·51291	1·48056	58·716
8.	III.*a*	2·25280	0·60726	0·00311	2·24969	0·60415	58·710
						Average..	58·709

* The weights of argentic bromide from which the sodic bromide was calculated were respectively 0·00520, 0·00516, 0·00615, 0·00687, and 0·00352 grm. in Analyses 1, 2, 3, 4, and 5. For Analyses 6, 7, and 8, the figures are given above.

In this series of results, the lowest is 58·696, while the highest is 58·719, a variation $\pm$0·012 from the mean. Adding all the determinations together, 24·31725 grms. of nickelous bromide yielded 6·52286 grms. of pure washed nickel and 0·02778 grm. of sodic bromide, calculated from 0·0507 grm. of argentic bromide. These two weights, taken in connection with the amount of bromine found a year ago, furnish a complete analysis of the best nickelous bromide which we were able to prepare. It must be remembered that 15·51556 grms. of the halide contained, according to two different methods, 11·34985 and 11·34979 grms. of bromine.

It has been already pointed out that this impurity of $\frac{1}{10}$ per cent of sodium would make no difference in last year's results if the "equivalent" of sodium equalled that of nickel. Since, however, it is somewhat less, slightly too much argentic bromide was obtained last year, and the atomic weight of nickel appeared lower than it really is. Assuming the amount of impurity to have been the same in last year's preparation as in this, 0·015 should be added to the atomic weight, in order to correct this error. The results of the four series, which represent the sum and substance of the present research, are then as follows:—Ratios (*e*) and (*f*) were obtained by cross-reckoning from the earlier ratios. The reason for thus re-stating the results is because this re-statement uses the weight of the nickelous bromide only as a constant, and not as a basis of calculation.

Complete Analysis of Nickelous Bromide.

	Per cent.
Nickel	= 26·824
Total bromine = 73·151 % = {Bromine combined with nickel}	= 73·062
Total impurity = 0·114 % = {Bromine actually found in impurity}	= 0·089
Total impurity = 0·114 % = {Sodium .. .. ..}	= 0·025
Total	= 100·000

(NOTE.—As has been detailed, some of the earlier preparations contained traces of sulphuric acid in addition. Since this is not taken into account in the average, the sum given is slightly too small, and is perhaps deceptive in its accurate showing. The flaw was eliminated as soon as it was discovered, therefore we had no means of finding the exact amount of the sulphuric acid, but in any case it was so small as to produce only a negligible effect on the result. From some experiments of Mr. Baxter's, it is safe to assume that this error could not have exceeded 0·005 per cent in the worst cases, and in the average it must be still much less).

		Atomic weight of nickel if O=16·000.
(*a*) Preliminary :	2AgBr : $NiBr_2$ ..	[58·695]
(*b*)	2AgBr : $NiBr_2$ ..	58·703
(*c*)	2Ag : $NiBr_2$ ..	58·704
(*d*)	($NiBr_2$—Ni) : Ni	58·709
[(*e*)]	2AgBr : Ni	58·706
[(*f*)]	2Ag : Ni	58·707
		59·706

If any assurance is needed that this average indicates very nearly the true atomic weight of nickel, the assurance may be found in the review of older work which follows. This review has been postponed until the close of the paper, in order that the methods might be judged in the light of our own experience with the subject.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 10th inst., His Grace the Duke of Northumberland presiding, on this the first General Monthly Meeting since his election as President. His Grace announced that the Hodgkins Medal, which is the first gold medal for scientific work ever given by the Smithsonian Institution, has been awarded to Professor Dewar, of the Royal Institution of Great Britain, in recognition of his discoveries in the liquefaction of air; and in so doing he congratulated Professor Dewar on this honour conferred on him, and also on the Royal Institution, which he regarded as specially gratifying as a sympathetic recognition of scientific work and discovery in this country, coming from the Great Nation of our own blood on the other side of the Atlantic. The following were elected Members:—Mrs. Aston, T. O. Belshaw, W. Hall, and Mrs. McClean. The special thanks of the Members were returned to Sir Benjamin Baker, K.C.M.G., for his donation of £50, and to Nobel's Explosives Company for a donation of £105, to the fund for the Promotion of Experimental Research at Low Temperatures.

THE NATURE OF VALENCE.

By F. P. VENABLE.*

THE term "valence" is variously defined as the "combining capacity," "capacity of saturation," "quantitative combining power," or "chemical value of the atom." It is well known that the introduction of this idea into chemistry was due to the development of the type theory, a system which had at first a purely empirical basis. Sixty years ago there was still some hesitation as to the acceptance of the atomic theory or the need for such a theory. Much use was made of the term equivalent, which had been Wollaston's expedient for avoiding the difficulties arising from the full adoption of the theory of atoms.

Wollaston had been himself very far from consistent in the use of the term. The numbers called by him "equivalent weights" were not unfrequently atomic and molecular weights, and fully as hypothetical as the so-called atomic weights of Dalton. In the later use of the term it signified solely the numbers obtained by analysis without the introduction of any theoretical considerations. Thus, on analysing ammonia, the ratio N : H :: 4·6 : 1 is gotten, and therefore the equivalent of nitrogen is 4·6. Strange to say the equivalent given by Wollaston corresponds with the present atomic weight, whereas the atomic weight given by Dalton corresponds with what would be the equivalent.

It is manifest that the idea of equivalents needed something more than the simple theory of atoms to make it clear and tenable. It embodied two distinct conceptions, and if we hold to an atomic theory we must introduce a further explanatory theory of the saturation capacity of these atoms. This is the theory of valence or quantivalence or atomicity, and without it the equivalents are purely empirical, and it is most difficult, if not impossible, to clear up the confusion connected with their use.

Returning now to the derivation of this idea of valence from the type theory, according to Wurtz ("Histoire des Doctrines Chimiques," p. 69) the conception of valence was introduced into the science in three steps. First there was the discovery of polyatomic compounds. This term was first used by Berzelius in 1827 (*Jsb. d. Chem.*, vii., 89), he applying it to such elements as chlorine or fluorine where he thought several atoms of these elements united with a single atom of another element. The term was later applied by Graham, Williamson, and others to compounds.

The second step was the reference of this polyatomicity to what was called the state of saturation of the radicals contained in these compounds. This was largely through the work of Williamson and Gerhardt.

Thirdly, this conception of saturation was extended to the elements themselves. This was chiefly due to the work of Frankland upon the organo-metallic compounds. And so valence has come to refer to the number of atoms with which a single atom of any element will combine.

This conception has then been one of slow growth, gradually incorporating itself into the science as the necessity arose of devising a suitable explanation for accumulated observations. It was a logical outcome of, and was evolved from, knowledge acquired step by step. It was no mere speculation or hypothesis, such as that of Prout, evolved by the brilliant fancy or imagination of one man, and suddenly appearing with scarcely a claim to foundation upon observed fact.

This conception enters into the chemical theory of to-day almost as fundamentally as the atomic theory itself. Its application is of every-day occurrence and of the most varied character, and yet chemists admit that the nature of valence is one of their chief puzzles, and they have advanced but little towards its solution during the past half-century. It is quite possible that the ideas to be advanced in the further discussion of this subject in this paper will meet with antagonism. Certainly they should be fully and freely discussed if they are worthy of it. I believe that they form a step toward the clearing up of the mystery of valence.

It is necessary, however, first to trace somewhat further the development of the original conception. One of its earliest and most important applications was to the study of the constitution of the compounds of carbon. Here Kekulé assumed for carbon a constant valence of four, and this idea is still dominant in the theories relating to the constitution of these bodies. It was quite natural, then, that the first belief should have been in a constant valence. It was speedily found, however, that in certain cases, as in the compounds of nitrogen and phosphorus, this belief was scarcely tenable. There were efforts at making it hold good, as, for instance, a distinction was drawn between atomic and molecular compounds, but all of these suggestions have been proved unsatisfactory.

We unquestionably have to account for the existence of a compound with three atoms and another with five atoms in the cases of nitrogen and phosphorus, and there are many similar anomalies. Here the valence seems to vary toward one and the same element. Cases might be multiplied to show also that it varies often towards different elements. Thus it frequently happens that the valence of an element towards hydrogen seems to be quite different from that exhibited toward oxygen. For a long time there was much straining to consider the valence of an element always the same; but this effort is, in large measure, abandoned now as unavailing, and chemists admit that valence is not constant, but variable, and may even vary towards one and the same element.

The doctrine of valence has had much added to it about bonds, affinities, and linkage, the necessity for which one may well question. Certainly the misuse of the word affinity here, seeing its other and greater use, should be earnestly discountenanced. I am inclined to think that the other terms bring in false and misleading ideas which should be carefully guarded against. At any rate all hypothetical talk about strong bonds, and weak bonds, double bonds and triple, is to be avoided.

If, then, valence varies, can it be an inherent property of the unchanging atoms? Experiments have shown that it varies with the nature of the combining element, that it varies with the temperature, and with other conditions. It is not dependent upon the atomic weight in the same sense as other properties are dependent upon it. Thus in the same group the valence remains the same whether the atoms weigh nine times as much as hydrogen or two hundred times as much.

We seem shut up to the conclusion that valence is not one of the primitive inherent properties of the atom, but is relative. It is rather to be regarded as the resultant of the mutual influence of the atoms of the combining elements. The clear grasping of the idea is an important step forward. Unfortunately the distinction is not always made nor consistently adhered to.

It may not be amiss to cite here the utterances of Lothar Meyer in regard to the question of a constant or variable valence ("Modern Theories of Chemistry," Eng. Trans., p. 303):—

"Since the aim of all scientific investigation is to exhibit the most variable phenomena as dependent upon certain active invariable factors taking part in them, and in such a manner that each phenomenon appears to be the necessary result of the properties and reciprocal action of these factors, then it is clear that chemical investigation would be considerably advanced were it possible to prove that the composition of chemical compounds is essentially determined by the valency of the atoms and the external conditions under which these atoms react upon one another. The first necessary step in this direction has been made

* Address (as Chairman) delivered before the North Carolina Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxi., No. 2.

in the attempt to explain the regularities observed in the composition of chemical compounds, by the assumption of a constant power of saturation or an invariable valency of the atom. The opposite and equally hypothetical assumption that the valency is variable leads to no advancement.

"The first step towards progress in this matter would be made if some hypothesis as to the cause of this variability were proposed. This difference between the two attitudes has seldom been properly realised. While some chemists, accepting the constant valency of atoms, have attempted to deduce the varying atomic linking from one distinct point of view, others have considered it sufficient to have assigned to the atom of a particular element in one compound one valency, and in another compound a different valency, according as this or that value appeared the most suitable, and thus to have given a so-called explanation of the composition of the compounds in question. In this way the fact has been overlooked that an arbitrary interpretation, carried out by means of chosen hypotheses, cannot be regarded as an attempt at a scientific explanation, but is nothing more than an expression of our ignorance of the causal connection of the phenomena. An explanation would require that the different valencies assigned to one and the same element, in different compounds, should be traced to a distinct cause. If, for instance, it is stated that carbon in carbon dioxide possesses double the valency which it possesses in carbon monoxide, such a statement is no explanation of the fact that an atom of carbon in the former compound is combined with twice as much oxygen as in the latter; for such a statement is merely a paraphrase which hides its incompetency by assuming the form of an explanation. Although this may be perceived without further remark, still it has frequently occurred during the past few years that similar paraphrases have not only been proposed, but also accepted as real explanations of such phenomena. Just as it was formerly supposed that the assumption of a vital force dispensed with a more complete investigation of the phenomena of animal life, so many chemists have of late thought that they possessed in 'variable valency' a means of explaining the varying stoichiometric relationships which would satisfy all claims. Such deceptions can only retard the advance of the science, since they prevent an earnest and thorough investigation of the question, whether each atom is endowed with a property determining and limiting the number of atoms with which it can combine, dependent upon the intrinsic nature of the atom, and like it invariable; or whether this ability is variable, and with it the nature of the atom itself."

It is not strange that this line of reasoning should lead Lothar Meyer to doubt the unvarying nature of the atom itself, and thus losing his grasp upon one invariable to make sure of another. He says "It is by no means impossible that the magnitudes which we now style atoms may be variable in their nature."

It will be an unfortunate day for chemists when the belief in the unchanging atom is given up. Chaos will indeed enter into all of our theories when this, the foundation rock, is left at the mercy of every shifting tide of opinion, and can be shaken by all manner of unfounded hypotheses.

The case cannot be so hopeless as to necessitate calling to our aid so dangerous a doctrine. Before turning to such an expedient let us first make all possible use of our atomic theory as it stands. The extension of this theory teaches that the atoms are endowed with motion, and this motion probably varies in velocity and phases with the different elements. So, too, when the atoms unite the resulting molecule has a certain motion peculiar to it, while the atoms composing it have an intra-molecular motion in which their original motions are probably modified by their influence upon one another. It is quite manifest, then, that a molecule, in order to exist, must maintain a certain equilibrium and harmony between these various motions, and that there can be all degrees of equilibrium from the very stable to that which may be upset by the least disturbing influence from without.

It seems to me that herein we have a full and satisfactory means of explaining the various problems connected with the conception of valence. The question as to whether the atoms of two elements will unite is decided by affinity, which is in some way connected with the electrical condition of those atoms. There is no apparent connection between this and valence. The number of atoms which enter into combination forming one molecule is purely a matter of equilibrium, and is dependent upon the motion of those atoms. Thus a phosphorus atom unites with chlorine atoms because of a certain affinity between them. The number of chlorine atoms with which it will unite depends upon the possibility of harmonising the respective motions. As the temperature may affect these motions, and also impart a more rapid molecular motion, it is evident that the harmony, or equilibrium, will depend upon the temperature, and that a temperature may be reached at which no harmony is possible, and hence no compound can be formed. The phosphorus atom mentioned can, as we know, form a stable molecule with five atoms of chlorine. On increasing the temperature this becomes unstable, and only three atoms can be retained. Neither with four atoms nor with two is there harmony of motion. A sufficiently high temperature may prevent any harmony of motion whatever being attained, and hence union may become impossible.

As to other influences than those of temperature, we can see that the equilibrium between the atom of phosphorus and the five atoms of chlorine may be upset by such a molecule coming within the influence, electrical or vibratory, of a molecule of water. The atoms must re-arrange themselves for a new state of equilibrium, and so an atom of oxygen takes the place of two atoms of chlorine, giving again a condition of harmony. In other cases the motion of the molecule of water may be of such a character as to directly harmonise with that of the original molecule, and so to enter into equilibrium with it, a definite number of such molecules of water affording a condition of maximum stability. This we call water of crystallisation. Such molecules would be more or less easily separated by an increase of temperature, and, where several molecules of water were attached, the highest temperature would be necessary for freeing the original molecule from the last water molecule.

A carbon atom finds its most perfect state of equilibrium where four atoms of hydrogen or their equivalents move in harmony with it. But there is a second state of equilibrium where only half that number of atoms are moving with it. This state does not seem to be a possibility where these are hydrogen atoms, but is readily possible where the equivalent number of oxygen atoms is concerned. Such a molecule, however, is always in a condition to take up additional atoms until its highest equilibrium is reached, and in doing this it proceeds by the regular steps needed for bringing about a harmony of motion. A molecule in a lower state of equilibrium we have become accustomed to call unsaturated, calling that one saturated which is in its highest state of equilibrium. The further application of this hypothesis is easily made, and need not be dwelt upon here. It will be helpful in many ways,

This theory of valence makes it clear why it should vary toward the same element under different conditions. It is also clear that it might vary towards different elements, as these are very possibly possessed of different motions. It is further evident that it is in accord with the conclusion that valence is not an inherent property of the indivdiual atom, but is the resultant of the influence upon each other of the combining atoms.

Only one point remains to be considered: Why do the elements of the same group have practically the same valence? The nearest answer to this, and it seems satisfactory, is that they are all possessed of the same

phase or kind of motion. In other words, the natural division into periods gives us seven or eight more or less different phases. These are, in large measure, independent of the atomic weight. And so the elements in any given group have the same tendency towards similar states of equilibrium in forming compounds with any other element, as hydrogen or oxygen. Some elements—as copper, mercury, tin, &c.—are peculiar in that they may change their phase of motion under certain influences, acting then as if they belonged to different groups, and entering into totally different states of equilibrium in forming their compounds.

Lastly, it is possible for a combination of atoms of different elements, as NH_4 or CN, to have such molecular and intra-molecular motion that, although not in a state of equilibrium themselves, they are capable of entering into such states just as the single atoms of elements do, having apparently similar valence.

I might develop this theory much further, but it is unnecessary now. Enough has been said to show that such an application of the atomic theory is legitimate and is most highly important as a step towards the clearing up of the problems springing from the conception of valence and from the Periodic System.

NOTE.—Since certain points in this paper require treatment at greater length than was practicable in an Address, it will be followed by a second paper elaborating such portions.

CORRESPONDENCE.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

SIR,—As I am the compiler of the tables printed in Dr. Lunge's "Treatise on Alkali Manufacture" quoted by Mr. H. A. Hooper in his letter to the CHEMICAL NEWS (vol. lxxix., p. 155), I may be allowed to point out that Mr. Hooper misunderstands the meaning of the soda figures given by the English alkalimetrical test. He is under the mistaken impression that the English test gives the *percentage* of soda in caustic soda calculated upon the 32 equivalent for soda; and that, consequently, if pure caustic soda be tested by English test-acid it will indicate 78·05 per cent of soda. This is not the case. If pure sodium hydrate, containing actually 77·5 per cent of soda be tested with English test-acid, it will indicate 78·52 English (or, as Dr. Lunge calls them, "Newcastle") degrees of soda—a number which is higher than the true percentage of soda by 1·02, as indicated by the tables.

English test-acid was used originally only for testing the percentage of soda in soda-ash and alkali; caustic soda not being at that time an article of commerce. The strength of the test acid was based upon the old and erroneous assumption that the equivalent of soda was 32, and that, therefore, pure carbonate of soda contained 59·26 per cent of soda. As a matter of fact, pure carbonate of soda really only contains 58·49 per cent of soda—the true equivalent of soda being 31 and not 32. English test-acid is therefore weaker than test-acid made on the correct equivalent of soda, and it indicates in titration an amount of soda greater than the true amount in the ratio of 59·26 : 58·49. When, later, caustic soda was manufactured, the same test-acid was—and still is—used for testing it as had been used for testing alkali, and the figures so obtained were commonly (but erroneously) called "percentages" instead of "English alkalimetrical degrees." It is true that when testing carbonate of soda English test-acid indicates the percentage of soda based on the 32 equivalent, but this is only true in the case of carbonate of soda. When any other compound of soda neutralisable by acid is tested by English test-acid, the English degrees of soda indicated are not percentages. It will be seen from the above that, in order to calculate the percentage of soda indicated by 31 equivalent test-acid into the corresponding English alkalimetrical degrees, it must be increased in the ratio of 58·49 to 59·26.

I quite endorse Mr. Hooper's opinion that it is highly desirable, for the sake of scientific accuracy, that the use of the 32 equivalent should be abolished.—I am, &c.,

JOHN PATTINSON.

75, The Side, Newcastle-on-Tyne,
April 4th, 1899.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

SIR,—Mr. H. A. Hooper, of Chicago, in the CHEMICAL NEWS of March 30th (vol. lxxix., p. 155) expresses his astonishment that a very serious error in the reduction of the true percentage of Na_2O to that calculated on the false 32 equivalent for Na_2O "should have been made and remained undetected by Prof. Lunge."

Mr. Hooper's astonishment ought to extend infinitely further; for precisely the same error must have been "made and remained undetected" by Mr. John Pattinson, who originally calculated (as stated in my book) the table quoted by Mr. Hooper, and by the thousands of chemists who have since that time used it.

But every reason for astonishment disappears to him who reads the explanation as given on page 106 of my book, just before the table itself. If Mr. Hooper had taken that trouble, he would have found what Mr. Pattinson, as well as myself and the rest of the world, understand by "Newcastle degrees" or "Tyne test"—something very different from Mr. Hooper's calculation. Those conventional degrees were originally intended for carbonate of soda, and have been later on applied (partly by extrapolation) to caustic soda. In the above-quoted place, Mr. Hooper will find that there are several other ways of using, or rather misusing, the 32 equivalent, and his own way of calculation adds one to the list.

In one respect I entirely agree with Mr. Hooper, viz., that the 32 equivalent should entirely disappear. On page 107 of my book he will find that I have done my level best in that direction for twenty years past; unfortunately not with sufficient success, since the "vested interests" of Liverpool are against it.—I am, &c.,

G. LUNGE.

Zürich, April 6, 1899.

ESTIMATION OF POTASH.

To the Editor of the Chemical News.

SIR,—With reference to my note on "The Estimation of Potash" (CHEMICAL NEWS, vol. lxxix., p. 135) and the remarks thereon (p. 154), I would say that the two processes are totally different; the essential part of mine being the addition of barium carbonate (already existing as such) to a slightly alkaline solution.

If ammonia is added to produce a *slight* alkalinity, and a *considerable excess* of barium carbonate used, the precipitation of sulphates is perfect. Probably this would not be the case if the ammonia were in considerable excess and only a small amount of the barium salt used; this, however, is guarded against if the directions are followed.—I am, &c.,

E. WIGHTMAN BELL.

High Bridge, Spalding, April 6, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 12, March 20, 1899.

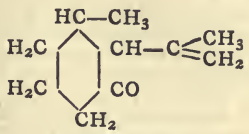
Action of Hydrogen Sulphide and of the Alkaline Sulphides on Double Cyanides; Cyanosulphides.—M. Berthelot.—The author states that, in presence of alkali, solutions of double cyanides are not precipitated by hydrogen or sodium sulphides. Freshly precipitated silver sulphide was washed with a solution of potassium cyanide, and filtered after a few minutes. The filtrate contained a considerable quantity of silver as double cyanide, together with potassium sulphide and potassium cyanide in excess. The addition of hydrogen sulphide gave no sensible precipitate, but on adding acetic acid, an abundant black precipitate of silver sulphide was obtained. The action of the hydrogen sulphide is dependent on the extent to which the potassium cyanide is present in excess; complete precipitation being effected without the addition of acetic acid if the cyanide is only in small excess. Hence, the stability of the argento-hydrocyanic acid present in the system increased with the excess of alkaline cyanide. Mercuric sulphide was not dissolved to an appreciable amount by potassium cyanide, but readily dissolved in sodium sulphide and in the absence of cyanides. From this solution it was re-precipitated on acidifying. The stability of the soluble double sulphide increases with the excess of the alkaline sulphide. On treating a solution of the double cyanide of zinc and potassium with hydrogen sulphide, the results obtained accorded with those of the double cyanide of silver and potassium under similar conditions.

An Isomer of Menthoxylic Acid.—Georges Leser.—Not suitable for abstraction.

Silico-tungstic Acid as Reagent for Alkaloids.—M. Duclaux.—The author has obtained well-defined stable salts of the alkaloids with silico-tungstic acid, which makes the latter valuable as a reagent. This acid, $12WO_3.SiO_2.2H_2O$, is the most sensitive of all the reagents, and the alkaloids are very easily extracted from the insoluble compounds it forms with them. The general type of these compounds is $12WO_3.SiO_2.2H_2O.4Alk.+nH_2O$. They are obtained as white or pale coloured precipitates from cold solutions of the salts of the alkaloids. They are almost insoluble in both hot and cold water, are unattacked by acids, and after calcination leave a residue of constant composition, consisting of silicic and tungstic acids. Oxidising agents decompose the silico-tungstates of the alkaloids. The alkaloids are re-generated by addition of dilute alkali, even of ammonia, the silicon and tungsten passing into solution.

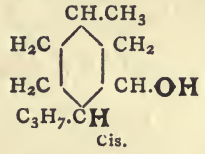
Liebig's Annalen der Chemie, April 18, 1898.

Research on the Terpenes and Essential Oils.—O. Wallach.—Pulegenic acid is an isomer of campholenic and phenolenic acids, and is produced by the action of alkalis on the dibromide of pulegone, $C_{10}H_{16}OBr_2$. It must be purified by distillation *in vacuo* immediately after its preparation. Hydrochloropulegenate of methyl, $C_{10}H_{16}Cl_2O_2$, treated on the water-bath with sodium and methanol, gives pulegenate of methyl, $C_{10}H_{15}O_2CH_3$, which distils at 89—90° under 10 m.m.; but, at the same time, there is partial saponification and formation of a lactone, $C_{10}H_{16}O_2$, isomerous with pulegenic acid. When we add a solution of BrOK to a concentrated solution of pulegenic acid in potash, an oil separates which is a bromised lactone. Although pulegone can be split up into methylhexanone and acetone, the body formed by the condensation of these two is not identical, but isomeric. The author assigns to this isomer the constitution—

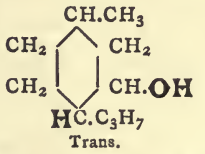


Orthoisopulegone.

On the Isomerics Cis- and Trans- in the Menthol Series.—O. Wallach and D. E. Werner.—Wallach has shown that, in the reduction of left-handed menthenoxime, a left-handed menthylamine is formed, while menthone furnishes—besides the left-handed amine—a right-handed menthylamine by the action of formate of ammonium. The difference between the right-handed or *cis*-menthol and the left-handed or *trans*-menthol is shown by the following formulæ—



Cis.



Trans.

On a New Camphor: Pinocamphone.—O. Wallach and J. A. Smythe.—Pinylamine, $C_{10}H_{15}NH_2$, obtained by the reduction of nitrosopinene, gives, with nitric acid, an alcohol, $C_{10}H_{15}OH$; and this, by oxidation, a ketone, $C_{10}H_{14}O$. The alcohol is pinocarveol, and the ketone pinocarvone. This latter easily gives a semicarbazone, $C_{10}H_{14}N.NH.CONH_2$, fusible at 204°, but not well crystallised. Pinocamphone is obtained by the reduction of nitrosopinene; it is an isomeric ketone of camphor. Its odour is somewhat like that of turpentine, and when warmed recalls that of menthol; it boils at 211—213° at the ordinary pressure; its density is 0·959; $n_D = 1·47273$.

On Phenone.—O. Wallach.—The author finds that phenone-carbonic acid, which he has attempted to purify, is in reality a mixture of two isomers. After having added water to the product of the reaction of CO_2 on phenone in the presence of sodium and absolute ether, the aqueous layer is exhausted with ether to remove the phenylic alcohol; the phenone-carbonic acid is then at once set at liberty by a quantity of acetic acid necessary to saturate the sodium used; the free acid is removed by means of ether, and the ethereal solution distilled *in vacuo*. There first passes over, between 80° and 150°, a liquid product; then, from 150° to 180°, a product which solidifies; after that, other products which will be examined later on. Pure α-phenone-carbonic acid, $C_{10}H_{16}(OH)CO_2H$, crystallises in acetic acid in transparent pointed prisms fusible at 141° to 142°; it distils without decomposition at 175° (11 m.m.). β-Phenone-carbonic acid crystallised in acetic acid in confused crystals melting at 76—77°; it is dextrogyre, but less so than the α-acid; it is also much less stable, and is decomposed by heat, losing either CO_2 or H_2O, giving either phenylic acid or anhydrophenone-carbonic acid. The isomerism between the α and β acids appears to be physical; α being a *trans*-compound, and β a *cis*. The products of oxidation with MnO_4K acid are the same—phenone is formed.

On Cinchotine.—Zd. H. Skraup.—A controversial paper, not suitable for abstraction.

Spontaneous Racemisation. — P. Walden. — The author shows that the rotatory power of the derived halogens is extremely unstable when the halogen atom is united directly to the asymmetric carbon. Racemisation is not always accompanied with decomposition.—*Berichte der Deutschen Chemischen Gesellschaft.*

MEETINGS FOR THE WEEK.

MONDAY, 17th.—Society of Arts, 8 (Cantor Lectures). "Leather Manufacture," Prof H. R. Procter, F.I.C.
TUESDAY, 18th.—Royal Institution, 3. "Zebras and Zebra Hybrids," by Prof. J. Cossar Ewart, M.D., F.R.S.
—— Society of Arts, 8. "Inlaying," by Stephen Webb.
WEDNESDAY, 19th.—Society of Arts, 8. "London's Water Supply," by Walter Hunter, M.Inst.C.E.
—— Microscopical, 8. "The Bioplasm of Man and the Higher Animals, and its Influence in Tissue Formation, Action, and Metabolism—a Microscopical Study," by Prof. Lionel S. Beale, F.R.S.
—— Institution of Mining and Metallurgy, 8. Presidential Address. "Notes on the Alleged Shortage in Cyanide Bullion," by C. W Merrill, Assoc.Inst.M.M. "Chemical Reactions involved in the Amalgamation of Silver Ores," Henry F. Collins, M.Inst.M.M,
THURSDAY, 20th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, M.A., LL.D., F.R.S.
—— Chemical, 8. "Some Dipyridyl Derivatives from Citrazinic Acid," by W. J. Sell, M.A., and H. Jackson, B.A., B.Sc. "Interaction of Mercurous and Mercuric Nitrites with the Nitrites of Silver and Sodium," by P. C. Ray, D.Sc. "Synthesis and Preparation of Terebic and Terpenylic Acids," by W. Trevor Lawrence. "Allotropic Modifications of Phosphorus," by D. L. Chapman. "β-Isopropyl-glutaric Acid," by F. H. Howles and J. F. Thorpe. "Ethyl-ammonium Sulphite," by Edward Divers and Masataka Ogawa. "Ethyl-ammonium Selenite and Non-existence of Amido-selenites (Selenosamates)," by Edward Divers and Seihachi Hada.
FRIDAY, 21st.—Royal Institution, 9. "Structure of the Brain in relation to its Functions," by Frederick Walker Mott, M.D., F.R.S.
—— Physical, 5. "Effect of a Solid Conducting Sphere in a Variable Magnetic Field on the Magnetic Induction at a Point Outside," by C. S. Whitehead, M.A. "Demonstration of Richards's Method of Standardising Thermometers," by R. A. Lehfeldt, D.Sc.
SATURDAY, 22nd.—Royal Institution, 3. "Machiavelli," by Louis Dyer, M.A.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Wolfram.—Can any correspondent inform me what are the present uses of this mineral and what price wolfram ore commands? —A. J. W.

TO CORRESPONDENTS.

Gas.—Richard B. Pilcher, Esq., Secretary of the Institute of Chemistry, 30, Bloomsbury Square, W.C.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2056.

ON CRUCIBLE STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

More remarkable results than my own have been obtained by M. Reyher, at the Baltic Works, in casting various hollow thin steel castings for the different and complicated fittings of marine water-tube boilers. Crucible nickel steel is used; the furnaces working with naphtha give a highly-heated soft steel, having good fluidity, which is so essential for the success of castings with a thin body.

The naval authorities prescribe the following tests:—Absolute resistance 28 to 35 tons per square inch, with an elongation not less than 14 per cent, in a length of 2 inches; bending test, 90° at 28 tons and 60° at 35 tons. Hollow castings for water-tube boilers are tested also under water-pressure; some of them must stand 450 lbs., other more responsible fittings 600 lbs. per square inch.

The Baltic Works steel castings not only fulfil such requirements, but give, with an absolute resistance of 32 to 34 tons, an elongation near and sometimes over 20 per cent. The bending tests are splendid, and cannot be compared with the results given by ordinary carbon mild steel. Nickel steel, containing about 2 per cent of nickel, is the best material for thin hollow castings.

In conclusion, I desire to give a preliminary notice that, for some time past, I have been experimenting to purify pig-irons from noxious elements, by means of hydrogen and some other gases. In preparing high-class crucible tool steel, wrought iron free from sulphur and phosphorus is necessary, but the price of such iron is often an obstacle. If we can get a quick method for removing sulphur and phosphorus from various pig-irons, we may say that such a problem will be beneficial to steel producers.

New Admiralty, April 6, 1899.

NEW METHOD FOR THE PRODUCTION OF HIGH TEMPERATURES, AND FOR THE PREPARATION OF DIFFICULTLY FUSIBLE METALS, FREE FROM CARBON.

By M. GOLDSCHMIDT.

The author first passes in review the different researches which have been made on the use of aluminium for the production of high temperatures, and then describes the method he has adopted.

We know that the combination of aluminium and oxygen gives rise to an extremely violent reaction, of which the temperature is estimated to be about 3000° C. To utilise this temperature practically, the principal difficulty seems to be in regulating the reaction by means of which the work is performed.

The first point to note is that there is no need to heat the whole of the reacting mass up to the temperature of ignition; it suffices to cause combustion at one single point. But in this there is still a practical difficulty to overcome. In the preparation of metallic chromium, starting with a mixture of oxide of chromium and powdered aluminium, this difficulty can be easily overcome by placing at a convenient point a small quantity of a mixture of aluminium with a more easily reducible oxide, or, better still, with a peroxide. Oxide of lead, oxide of copper, permanganate of potash, and other substances, may be used for this purpose.

The great advantage of this method is that it enables us to prepare the pure metals, free from aluminium; the only precaution to take is to employ a slight excess of the oxide to be reduced.

The process is capable of two principal applications. In the first place, the heat given off by the combustion of a mixture of aluminium and a suitable oxide can be used simply as a source of heat (for soldering, welding, &c.). In the second place, the reducing power of aluminium, at a high temperature, can be utilised in the preparation of pure metals and of alloys. In both cases the method of working is practically the same.

If we only desire to produce a moderate heat the reacting mass is diluted by the addition of some inert substance, which at the same time prevents the fusion of the mixture. A very good mixture of this nature is composed of aluminium and some cheap oxide, such as oxide of iron, sand, &c., to which may be added lime, magnesia, &c. If, on the contrary, we wish to produce a reduction to the metallic state, we must be careful not to use too great a proportion of oxide, in such a manner that the heat given off by the reaction will melt not only the reduced metal, but also the slag. This latter will then protect the metal against any oxidising action of the air.

I now give a few experiments which form so many interesting applications of this process.

A rivet, weighing 3 kilogrms., such as are employed in bridge-making, is imbedded in a mixture of oxide of iron, sand, and aluminium powder. The whole is plunged in sand contained in a wooden box. On the top of the aluminium mixture, which must just emerge from the sand in the box, we place a small lump of a mixture of aluminium powder and an easily reduced oxide, in which is fixed the end of a short piece of magnesium ribbon. The reaction is started by lighting the free end of the magnesium, and we then immediately place more sand on the top of the mixture, so that as little heat as possible may be lost. If, at the end of a few moments, we empty out the contents of the box, the rivet will be found to be quite red-hot and ready to be forged.

Working in an analogous manner, we can weld together steel tubes of 2·5 c.m. diameter, and the expense will not be more than twopence. We can even fuse together two bars of soft steel.

By diminishing the quantity of inert material used in the preceding experiments, iron can be easily melted.

To reduce oxide of chromium it must be mixed with a suitable quantity of aluminium, and placed in a crucible brasked with magnesia. The reaction is started in the manner described above, and we go on adding the mixture until the crucible is full. After cooling, we break the crucible and take out the ingot of metallic chromium. The author has presented to the German Electrochemical Society a block of metallic chromium weighing 25 kilogrammes, prepared by this method.

By arranging two orifices in the crucible, one for the introduction of the mixture and the other for the escape of the metal, we can make the operation continuous, as in the electric furnace.

According to the author, the temperature obtained under these conditions is higher than that realised in the electric furnace, and we can reduce a given quantity of a metallic oxide in a much shorter space of time, and, further, the metal obtained is entirely free from carbon and carbides. The slag (alumina) obtained can be used over again for the production of aluminium, or it may be utilised as a polishing material; it has, in fact, great advantages over emery.

Nearly all the metals can be reduced by this method, and the return is almost theoretical. We can also prepare alloys such as those of chromium and manganese, copper and chromium, &c., by the same method.

For the preparation of pure metals it is necessary to

use only pure aluminium, but for simple heating operations the metal at 50 per cent purity will suffice. Besides the oxides we can also reduce the oxysalts of certain metals.

The author looks upon aluminium as a *heat accumulator*, since its utilisation as a reducing agent allows of the regeneration of a quantity of energy, corresponding to that required for its precipitation.—*Zeits. für Electrochemie*, 1898, iv., 21, p. 494.

THE ESTIMATION OF LEAD IN ITS ORES.

By F. MOLDENHAUER.

There are a number of well-known methods giving perfectly exact results, but they nearly all necessitate the use of a large amount of apparatus, reagents, &c., which prevents them being used universally. I propose describing a method I have devised and which has given me excellent results.

In the case of ores containing less than 30 per cent of lead, we take 2 grms. of the material and reduce it to a fine powder. We then boil with strong hydrochloric acid until the attack is complete and no more bubbles of gas are given off. When we have to do with ores very rich in antimony, it is better to evaporate three or four times, in the presence of strong hydrochloric acid; in this way all the antimony is eliminated. We then add nitric acid, drop by drop, and evaporate to dryness rapidly to destroy the sulphides.

The residue is taken up with the necessary quantity of hydrochloric acid, 80 to 100 c.c. of water are added, the whole brought to a boil and filtered as hot as possible into a flask or a matras. Wash, as hot as possible, with water acidulated with hydrochloric acid, to dissolve all the chloride of lead. The filtrate is heated, ammonia added (but not enough to produce a precipitate), and submitted while warm to the action of sulphuretted hydrogen. The precipitate formed is thrown on a filter and washed, first with water and then with warm sulphide of ammonium; it is compressed between two sheets of filter-paper, and placed in a porcelain crucible of 50 or 60 c.c. capacity, which must be covered with a watch-glass, after having added some concentrated nitric acid. We then evaporate to dryness over a small flame, and calcine in the presence of air; allow to cool, and repeat the same treatment; after this we add concentrated sulphuric acid, bring to boiling for a moment, and after complete cooling add water, boil again, then throw the sulphate of lead formed on a filter. After desiccation, remove the sulphate of lead from the filter and place it in a porcelain crucible, burn the filter separately, and weigh the whole after calcination.—*Chemiker Zeitung*, 1898, p. 256.

THE ESTIMATION OF PHENOLS IN DISINFECTANTS IN THE PRESENCE OF SOAP.

By M. W. SPALTEHOLE.

Several different methods have been proposed for the estimation of phenols in the presence of soap.

A. Blomquis recommends simply submitting the product to distillation at 210°. But, as he himself admitted, this separation is not sufficient to isolate the whole of the phenols. To obviate this inconvenience he suggests a correction, the value of which is, however, very problematical.

M. Fresenius and C. Martin add a mineral acid to the product, distil the liquid in a current of steam, and estimate the phenols in the distillate by Koppeschaar's method.

The author has noticed that the addition of a mineral acid to the product is not necessary in the case of disinfectants which have a neutral reaction, and therefore contain free phenol, as, for example, creoline, lysol, soluble cresol, &c. He estimates the phenols in these products in the following manner:—The material to be analysed is heated, in an iron vessel for preference, to a temperature of 200°, a current of steam is passed through it, and the temperature increased to 220°: this operation is continued until the current of steam no longer carries over any oily drops. If we have to deal with products containing oleic soaps the temperature must not exceed 210°, for at about 220° these soaps are decomposed by steam, and oleine passes over into the distillate. Resin soaps do not decompose even at 220°. The distillate contains either phenols only, as with lysol, or phenols mixed with the hydrocarbons of the tarry series, as with creoline. The phenols thus isolated can be estimated either directly or in the combined state. The simplest method consists in exhausting the distillate with benzene, and estimating the phenols in the benzenic extract by means of a titrated solution of caustic soda.

The author has himself prepared and analysed a series of products by this method. The results obtained were at the most not lower than 0·5 to 1 per cent of the actual proportion of phenols present in the soap. These results may be considered as sufficiently exact for determining the quality of commercial disinfectants.

The proportion of lysol in phenols varied in the different products examined, from 40 to 60 per cent.

As for commercial creolines, the author has found that the proportion of phenols present varies from 0 to 20 per cent. One creoline contained as much as 28 per cent of phenols, but it did not give a good lather with water. In creolines giving a good, persistent lather, the proportion of phenols present does not exceed 18 per cent. If we take the proportion of phenols present as a basis for estimating the disinfecting power of the products, it must be remembered that lysol is much more powerful than creoline. However, in this latter it is not only the phenols that act as antiseptics; they also contain hydrocarbons of the tarry series, which exercise, according to the researches of Prof. Forster, an appreciable bactericidal action.—*Chemiker Zeitung*, 1898, p. 58.

ON THE METHODS EMPLOYED IN THE ANALYSIS OF COMMERCIAL AMMONIA.

By A. LUNGE and W. HEFTER.

A certain number of papers have been recently published having for their subject the analysis of commercial ammonia.

Lange and Hertz (*Zeitschr. f. Angew. Chem.*, 1897, 224) collected the ammonia in an open receiver, while Bunte and Eitner (*Journ. f. Gasbel und Wasservers.*, 1897, 174), the same as Urban (*Chem. Zeit.*, 1897, p. 720, and *Moniteur Scientifique*, 1898, p. 68) put the reservoir in direct communication with a closed vessel, and filled this latter by pressure. The method utilising a closed vessel would have the advantage of preventing any error resulting from evaporation during the collection of the sample.

We now propose to review these different methods.

We will first briefly describe the Bunte-Eitner method. Into a glass pipette furnished with a stopcock at each end, we pass the ammonia directly from the reservoir and weigh it. We then place the pipette in a vertical position and connect it with three absorption-tubes filled with solid potash, the weights of which have been accurately determined. We then open the upper stopcock of the pipette, so as to allow the gaseous ammonia to slowly traverse the potash-tubes. After the evaporation of the liquefied ammonia we place the pipette, in a horizontal

position, in a hot-air oven, which must be gradually heated to 70—80°; at the same time we pass a current of dry air, free from carbonic acid, through the apparatus for some time.

If it were true that this method gives accurate results, we ought to find the impurities which accompany the ammonia in the absorption-tubes, such as water, pyridine, naphthalene, ethylic alcohol, acetonitrile, benzol, &c. But in practice this is not the case; all these bodies are volatile at 70—80°; they are carried away with the current of gas, and are only found in minute quantities in the absorption apparatus. It is therefore evident that the method in question does not give anything like exact results.

It is true Urban has improved the Bunte-Eitner process, inasmuch as, leaving the absorption-tubes alone, he weighs the residue from the evaporation, after heating to 30° only. It is a fact that a certain quantity of ammonia remains dissolved in this residue, but the resulting error is so small that it may be neglected.

For the purpose of comparing Urban's method with that of Lange and Hertz we have prepared different mixtures, of which the composition was accurately known. These mixtures were made with pure ammonia (with 0·2 per cent residue), with benzol, alcohol, pyridine, and water, and with residues from various samples of ammonia. The following are the results we obtained:—

Nature of impurity.	Calculated p.c.	Found afterwards. Lange and Urban.	Lange and Hertz.	Per cent. Lange and Urban.	Lange and Hertz.	Mean.
Benzol	1·5	0·99	1·7	66	113	—
,, ...	1·5	0·75	1·5	50	100	—
,, ...	1·5	1·13	1·5	75	100	—
,, ...	1·5	0·77	1·0	51	67	—
,, ...	1·5	0·76	1·0	51	67	—
Pyridine ..	1·0	0·65	1·2	65	120	—
,, ...	1·0	0·70	1·1	70	110	—
Water	1·1	0·91	1·2	83	109	—
Alcohol	1·0	0·80	1·6	80	160	—
,, ...	1·0	0·79	1·8	79	180	—
Alcohol and acetonitrile .	1·0	0·79	1·5	79	150	—
Alcohol and benzol ..	1·3	0·79	1·4	61	108	—
Benzol and pyridine ..	1·0	0·80	0·9	80	90	—
,, ,,	1·0	0·66	1·1	86	110	—
Residue A ..	1·0	0·54	1·1	54	110	82·0
,, ..	1·7	1·41	1·9	83	112	97·5
Residue B ..	1·1	0·74	1·5	67	136	101·5
,, ..	2·2	1·54	2·8	70	127	98·5
,, ..	2·7	2·04	3·1	76	115	95·5
Residue C ..	1·0	0·80	1·3	80	130	105·0
,, ..	1·7	1·33	2·2	78	130	104·0
Mean of all the samples	—	—	—	72	120	96 0
Mean of the 7 last samples	—	—	—	72	123	98·0

It will be seen that neither of these two methods is rigorously exact; Urban's method gives figures which are too low, while those of Lange and Hertz are too high. As there can be no loss of ammonia in the taking of the sample, it must be admitted that a portion of the impurities has been mechanically carried over by the ammonia gas. The quantity of these entangled impurities varies considerably from one sample to another—it depends on the nature of the body present. Benzol and pyridine are the most easily carried over, while alcohol and water are more difficult; among the mixtures, that composed of equal parts of alcohol and pyridine is the most difficult to be carried over.

These considerations enable us to explain how it is that sometimes the Lange-Hertz method gives perfectly exact results. We have also a word to say about the method used in America and Australia for the examination of commercial ammonia. In these countries it is required that the ammonia, transferred from the reservoir to an open vessel, should have a boiling-point of 33·7° C.; a higher boiling-point denotes a less pure product. But we have observed that this method is very unsatisfactory, and that it does not enable one to distinguish with certainty between a product containing 0·1 per cent of impurity and another containing 1·0 per cent.

Thus all the methods which have up to now been recognised in the analysis of commercial ammonia are sullied with grave errors, and cannot be used when scientifically exact results are required.

But, we may ask, is it really necessary, commercially, to have absolutely correct results? Liquid ammonia is almost exclusively used for the manufacture of ice, and it is evident that its refrigerating action will be the greater the purer it is; but, on the other hand, we do not think that small quantities of impurities can have any very serious action. It is not really indispensable to know whether a given ammonia contains 1 per cent or 1·2 per cent of impurities; we must, however, insist that such impurities should not exceed a maximum limit, which will vary from one case to another, according to the wants of the consumer. Now to determine the permissible amount of these impurities, which of these two methods in question should we advise? One gives too high results and the other too low; but the mean of the two more often approaches the truth, as will be seen in the above table.

The Lange-Hertz method is very easy to perform, and we do not hesitate to recommend it, whatever may be said for Urban's, until we have succeeded in finding a really exact method.—*Die Chemische Industrie*, 1898, p. 2.

A NEW METHOD FOR THE DETERMINATION OF ZINC.

By A. C. LANGMUIR.

PRACTICALLY two methods only are in general use for the gravimetric determination of zinc. Of these the carbonate method, with its many imperfections, is being displaced by the phosphate method, at least in this country.

With care the latter will yield excellent results. In our practice it is customary to use ammonium phosphate in place of the usual sodium salt (Garrigues, (*Journ. Amer. Chem. Soc.*, xix., 934), and after the precipitation of the phosphate to destroy the slight excess of ammonia remaining after heating on the water-bath, by the cautious addition of dilute acetic acid. Under these conditions the filtrate is free from zinc.

Directly igniting the sulphide and filter, and weighing as oxide or sulphide, has been used, but is open to serious objection if the amount of zinc is at all large.

As far as we are aware no one has proposed the solution of the sulphide in nitric acid, the evaporation of the solution so obtained, and the conversion of the residue to oxide by ignition. As a second precipitation and washing is avoided it is quicker than the carbonate or phosphate methods, and is preferable to the latter in that the impurities almost invariably present in the zinc precipitate may be easily determined and allowed for.

The sample of ore for analysis (½ to 1 grm. according to its zinc content) is dissolved, and the metals precipitated by hydrogen sulphide separated by the usual methods. After expelling hydrogen sulphide the solution is coloured by bromine water, and the iron and any manganese present are separated by ammonia. The precipitate is dissolved in hydrochloric acid, and the precipitation is repeated a second or third time if necessary.

If the ore is one which is known to be free from lime and magnesia, the combined filtrates may be boiled down

immediately, with the addition of an excess of nitric acid, to destroy chlorides and ammonium salts. After the removal of the chlorine, the solution is transferred to a weighed platinum dish, evaporated to dryness, ignited, and weighed as oxide.

The troublesome filtration and washing of the zinc sulphide should be avoided if possible. In our opinion better results are obtained by the ferrocyanide titration of the solution of the unwashed sulphide than by any gravimetric method involving the filtration and *washing* of this precipitate.*

The zinc is best precipitated as follows:—Acidulate the warm ammoniacal filtrate from the iron with hydrochloric acid, add a few drops of sulphurous acid to neutralise the bromine set free, then three or four drops of methyl orange.† Neutralise with ammonia carefully, and add ammonium sulphide drop by drop, with constant stirring, until a drop of the solution gives a dark colouration with a drop of dilute ferric chloride solution on a porcelain plate, showing a slight excess only of ammonium sulphide. The liquid is now warmed on the water-bath until the sulphide is settled, and is filtered through a double-ribbed filter. Under these conditions a clear filtrate is invariably obtained, but if washing is attempted the filtrate is frequently cloudy.

We therefore dissolve directly, without washing, in hot nitric acid (1 : 3), or in dilute hydrochloric acid if cobalt or nickel are present, and correct the weight of the oxide subsequently found for the small amounts of lime or magnesia present. It is well to make a qualitative test for these elements in the filtrate from the sulphide. If absent or in small amount the correction in the weight of the oxide may be omitted.

The solution is boiled down rapidly in a casserole, with the addition of nitric acid to expel chlorides. When almost dry the contents are rinsed into a weighed platinum dish or crucible. The evaporation is continued on the water-bath or hot plate until dry, when the nitrate is ignited at the full heat of the Bunsen burner. As some zinc sulphate, which is always present, is not decomposed at this temperature, it is necessary to break up this compound by intense ignition over the blast-lamp. Any lumps should be first broken up by a blunt glass rod. Ammonium carbonate may be used, but is liable to occasion some loss.

It may be possible, by igniting at a low heat, to weigh the zinc as sulphate, after evaporating with sulphuric acid. We are working on this now.

After weighing, the oxide is dissolved in hydrochloric acid, and the small amount of iron always present, thrown down with ammonia, ignited, brushed into the tared watch-glass in the balance, and weighed directly. The filtrate is acidulated with hydrochloric acid, heated to boiling, and tested for sulphates with barium chloride. A slight precipitate will usually form, but this may, in general, be neglected if the ignition has been properly performed. If in weighable amount it may be treated as in the case of the iron, calculated to sulphur trioxide, and, together with the ferric oxide, deducted from the weight of the impure oxide.

If lime or magnesia were present, the filtrate from the iron should be divided into equal parts, one of which is tested for sulphates and the other for lime and magnesia, by throwing out the zinc as sulphide, and testing the filtrate by the ordinary methods. As a rule this is unnecessary unless the lime or magnesia is present in large amounts, for the sulphide is precipitated in dilute solution and the amount of lime remaining in the unwashed sulphide would usually be very small.

The correction for impurities may seem tedious, but in reality it is quickly carried out. Richards has found that zinc oxide obtained by the ignition of the nitrate contains a little occluded nitrogen. This would only amount to a few tenths of a m.grm, and may be neglected unless unusually accurate work is called for.

For the determination of zinc in alloys containing copper, tin, lead, iron, and zinc, dissolve in nitric acid, evaporate to dryness, and take up with nitric acid if tin be present. Filter and separate copper and lead simultaneously by electrolysis. The solution should contain 5 to 10 c.c. concentrated nitric acid in 150 to 200 c.c. water. After removing and washing the electrodes carrying copper and lead, the solution is evaporated to dryness in a weighed platinum dish and the residue ignited and weighed. Dissolve in hydrochloric acid and separate the usually small amount of iron present by ammonia. Ignite, weigh, and deduct from the weight of the zinc oxide. If nickel be present the weight of the combined oxides may be taken and the nickel afterwards determined, when the zinc may be found by difference.

Zinc in pure spelters is best determined by difference. In impure samples it is sometimes more convenient and equally accurate to determine zinc directly. Dissolve ½ grm. in nitric acid and separate the lead electrolytically in a solution carrying 10 per cent nitric acid. Use the platinum cylinder in this case to collect the lead peroxide. Evaporate the solution to dryness in a weighed dish, ignite, and weigh. Dissolve in a little hydrochloric acid, reduce with 2 to 3 grms. granulated zinc, add sulphuric acid to complete the reaction, dilute with ice-water to 1 litre, and titrate with permanganate. Correct for the amount of iron found. If cadmium, arsenic, or other impurities were present in more than traces the above method would be inapplicable unless modified to include treatment by hydrogen sulphide.

We have not found time to make an extended series of tests of this method, but, in numerous analyses of ores and the complete analysis of alloys in which in duplicate analyses the zinc was determined by the well-known methods, the author has convinced himself of the accuracy of the method.—*Journal of the American Chemical Society*, vol. xxi., No. 2, p. 125.

* C. F. McKenna has suggested to the author that the addition of a little paper pulp to the solution prior to filtration will insure a clear filtrate. If some asbestos is stirred into a cloudy zinc filtrate, and the solution passed again through the paper, the filtrate will generally be clear. But in any case the slow washing of the precipitate exposes us to a loss through oxidation.

† The methyl orange used in exactly neutralising the solution prior to the ferrocyanide titration, and which slightly interferes with the delicacy of the end-reaction, may be readily destroyed after the acidulation by pouring into the beaker a little bromine vapour and stirring this in.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several

samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the past month has shown a very great deficit. The actual rain that fell was 0·25 inch; the thirty years' average is 1·50 inches. This gives a deficiency of 1·25 inches, changing the previous excess of 0·85 inch into a deficiency of 0·4 inch, or 7·3 per cent on the thirty years' average fall.

Rain fell on six days only, viz., on the 4th, 8th, 21st, 25th, 28th, and 30th. The heaviest fall was 0·08 inch on the 8th.

Our bacteriological examinations of 253 samples have given the results recorded in the following table; we have also examined 44 other samples, from special wells, standpipes, &c., making a total of 297 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	2032
New River, filtered (mean of 25 samples) ..	35
Thames, unfiltered (mean of 26 samples) ..	12133
Thames water, from the clear water wells of five Thames-derived supplies (mean of 126 samples)	28
Ditto ditto .. .. highest	280
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	3977
River Lea, from the East London Company's clear water well (mean of 25 samples) . ..	33

The chief characteristic of the Metropolitan water supply this month has been its exceptional microbic purity. While in February the raw Thames-water contained over 23,000 microbes per cubic centimetre, yielding filtered water containing an average of 54 microbes, the unfiltered Thames in March contained an average of 12,000 microbes, and the filtered water 28 microbes per cubic centimetre. The improvement in the River Lea is equally marked. In February the unfiltered Lea showed an average of 7481 microbes, reduced by filtration to 68; while during March the average number of microbes in the Lea, unfiltered and filtered, have been respectively 5977 and 33. This marked improvement in the river waters is certainly connected with the deficient rainfall of the past month, as detailed in a previous part of this report,

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

A REVISION OF THE ATOMIC WEIGHT OF NICKEL.*

Second Paper.—The Determination of the Nickel in Nickelous Bromide.

By THEODORE WILLIAM RICHARDS
and
ALLERTON SEWARD CUSHMAN.

(Concluded from p. 175).

A Brief Criticism of Earlier Work.

The atomic weights of nickel and cobalt have each been the subject of a score of different researches since the problem was first attacked by Rothoff in 1818. These investigations have not only led to exceedingly discordant results, but have also given rise to several interesting and important controversies. As a chronological list is given in our former papers (*Proc. Amer. Acad.*, xxxiii., 97, 115), there is no need of repeating it here. For the purpose of criticism one should rather classify the investigations according to the methods used in them.

The most direct method of determining the atomic weight of nickel is obviously the reduction of nickelous oxide, for in this way the ratio between nickel and oxygen, the usually accepted standard of atomic weights, is settled at once. Russell; Zimmermann; Mond, Langer, and Quincke; Schützenberger; and Krüss and Schmidt used this method with varying degrees of success.

	Result.
1863 Russell (*Journ. Chem. Soc.*, [2], i., 51)	Ni=58·743
1886 Zimmermann (*Liebig's Annalen*, ccxxxii., 324)	Ni=58·694
1890 Mond, &c. (*Journ. Chem. Soc.*, lvii., 753)	Ni=58·580
1892 Schützenberger (*Comptes Rendus*, cxiv., 1149)	Ni=58·515
1892 Krüss and Schmidt (*Zeit. Anorg. Chem.*, ii., 235)	Ni=57·5 to 64·(!)

Of these five investigations, the third was hastily undertaken only to show that nickel which has been vaporised as nickel carbonyl is essentially similar to the ordinary material; the fourth included only two determinations made with oxide undoubtedly containing traces of sulphate, and the last was hopelessly faulty for reasons already discussed. Hence as exact criteria we may reject these three at once, and turn back to the much more carefully executed work of Russell and Zimmermann.

Russell showed that when the higher oxides of nickel and cobalt are ignited in an inert atmosphere, oxygen is driven off and the monoxide remains. His materials were contained in a Rose crucible of platinum; and after igniting the oxides in a stream of carbon dioxide, he reduced them in a stream of hydrogen. His nickelous oxide was very carefully freed from all extraneous matter except the insidious impurities derived from his glass vessels, against which no precautions were taken. A careful study of his work shows that this is the most serious cause of error likely to affect his final result, but that it was probably in part counteracted by the presence of occluded gases in the oxide; hence we have good reason to believe that this result is probably somewhat, but not much, too high.

Zimmermann followed essentially the same method as Russell. From ten exceedingly concordant analyses he deduced the value 58·694* for nickel—a value slightly lower than Russell's 58·743. His work also was carried out with great care, and the effort was made to avoid the occlusion of alkaline impurities by precipitating the final hydroxide of nickel with pure oxide of mercury, thus doing away with the use of an alkaline precipitant. This improvement also lessened the danger of Russell's other chief error, and at the same time introduced yet another with an opposite tendency—the inclusion of mercury. Hence it is not surprising that his result should be somewhat the lower of the two. An unprejudiced critic cannot but consider Zimmermann's work as the best among the older researches, and it is pleasant to call attention to the fact that Zimmermann's result differs by only the fiftieth of one per cent from ours. The reason why this method gives a result more satisfactory in the case of nickel than in that of cobalt is probably because cobaltous oxide is so much more readily raised to the higher stage of oxidation. Both Russell's and Zimmermann's work may have been slightly vitiated by the presence of occluded hydrogen in their nickel; but it is impossible now to appraise

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No 13, February, 1899.

* Krüss and Alibegoff, who published Zimmermann's result, after his death, unwisely omitted to apply the correction to the vacuum standard. This omission has been supplied above.

the error involved, because the phenomenon is so irregular.

It is convenient to class together five more investigations which appeared between 1857 and 1871, viz.,—

1857	Schneider (*Pogg. Ann.*, ci., 387; cvii., 616)	58·07
1858	Marignac (*Arch. Sci. Nat.*, Nouv. Sér., i., 375)	58·90
1860	Dumas (*Liebig's Annalen*, cxiii., 25)	59·02
1866	Sommaruga (*Sitzber. Wien. Acad.*, liv., [2], 50)	58·03
1871	Lee (*Am. Journ. Sci.*, [3], ii., 44)	58·01

In the light of present knowledge concerning the possibilities of accurate quantitative work, these contributions may be dismissed with few words. Marignac showed that Schneider's oxalate contained occluded impurities, and Schneider showed that Marignac's chloride could hardly have been both anhydrous and free from oxide. Our own experience entirely confirms both of these criticisms. Dumas's lack of ability to determine chlorine with accuracy throws out his analysis of the chloride at once, even if one is credulous enough to believe that the chloride itself was pure. Sommaruga precipitated sulphuric acid from nickelous potassic sulphate as baric sulphate—a method now ostracised except for crude work. Lee's work was wonderfully accurate considering the small quantities of materials which he used, but these quantities were so microscopic, and his compounds were so complex, that one could not have been expected to improve much upon his error of 1 per cent without a radical reformation of method.

Within this same period appeared another paper by Russell, elaborated as carefully as his previous one, but depending upon a less satisfactory process. The hydrogen evolved by the action of nickel upon hydrochloric acid was measured. Many uncertainties combine to make this method of little value, so that the result (58·77 ?) does not carry with it much weight.

Three chemists in three different decades, Marignac, Baubigny, and Schützenberger, have attempted to solve the question by the quantitative ignition of nickelous sulphate:—

			Greatest difference from mean.
1858	Marignac (*Arch. Sci. Nat.*, Nouv. Sér., i., 374)	Ni=58·70	±0·15
1883	Baubigny (*Compt. Rend.*, xcvii., 951)	Ni=58·73	±0·002
1892	Schützenberger (*Compt. Rend.*, cxiv., 1149)	Ni=58·65	±0·075

The three investigations agreed fairly well upon an average result, 58·71 (Clarke, "Re-calculation," top of page 302), Baubigny's being by far the most satisfactory. This method is one involving two errors which nearly counterbalance each other; the sulphate has a tendency to retain water, while the oxide almost invariably retains sulphuric acid. For this reason, the method gives results which approximate closely to the truth (see "A Table of Atomic Weights," *Proc. Amer. Acad.*, xxxiii., 297; Chem. News, lxxviii., 182). Here, again, we have a support for the conclusion that the value in question cannot be far from 58·7.

All the published work upon the subject has now been referred to, except some early work of Rothoff, Erdmann and Marchand, and Deville (see Clarke, "Re-calculation," p. 291), which deserves no more than a passing mention, and the more recent researches of Winkler. Küss's misguided work has been sufficiently dissected by Winkler's able but unsparing criticism (*Zeit. Anorg. Chem.*, iv., 10) and in the experimental part of this paper. The only points not covered by Winkler—the rose-coloured flame test and the solubility of nickelous hydrate—are explained in the foregoing pages.

The work of Winkler is surprising in its variety and in the ingenuity of his methods, but unfortunately it is equally surprising in the wide range of 1 per cent between his several results. His earliest work (*Zeit. Anal. Chem.*, 1867, vi., 18; Ni=59·45, Clarke), depending upon the reduction of sodic aurochloride by nickel, giving the extremely high value 59·45, is obviously at fault. Winkler himself ignores it in his discussion (*Zeit. Anorg. Chem.*, iv., 10; viii., 1), so that further criticism of it may well be omitted.

Winkler's two later investigations, carried out only a few years ago, gave results much lower and more satisfactory. In his first revision, he weighed nickel, converted it into chloride, and determined the chlorine both gravimetrically and volumetrically (*Zeit. Anorg. Chem.*, 1893, iv., 10), he wisely regulated his operations in such a way as to avoid the use of alkalis; but in his ardour to escape this danger he encountered others as serious. It is highly unlikely that the electrolytic nickel, dried at only 50° while adhering to the dish, could have been free from impurities, as we have already shown in the experimental part of our paper. Indeed, he confessed in a later paper (*Zeit. Anorg. Chem.*, viii. 4) that the electrolysis of cobalt at any rate is very far from being as accurate a process as it is sometimes supposed to be. The report of the acid reaction of the chlorides of these metals would have had more significance if the indicator had been named, for the salts destroy the magenta of phenolphthalein only because they remove the hydroxyl ions from the solution. Both chlorides are perfectly neutral to methyl-orange. A loss of chlorine during the drying of either chloride would, of course, raise the observed atomic weight; and while in the case of nickel the loss was so small as not to have produced a visible cloudiness, no proof is offered that no loss took place. In the case of the cobalt "eine gewisse, aber so schwache Trübung, dass sie, wie man zu sagen pflegt, nicht 'blank' erschien" involved a loss of as much as 1 per cent of material, and it is well possible that a smaller but still important amount of basic salt may have escaped notice in the case of the nickel. Our own experience with the halides of both metals convinces us that it is quite impossible to obtain them pure and dry by evaporation to dryness in moist air. Turning now to the determination of the chlorine in the salts, we find other grave flaws. No account was taken of the solubility of argentic chloride in the gravimetric work, and several milligrms. must have been washed away by the hot dilute nitric acid used as a washing fluid. One is surprised, too, to find that the antiquated process of burning the filter was adopted, instead of Gooch's admirable substitute. In the volumetric work again the solubility of argentic chloride was overlooked, although it produces a most injurious effect on the method of Volhard (*Proc. Amer. Acad.*, xxvi., 34; and xxix., 67). It is, indeed, surprising to see so eminent a chemist using volumetric methods at all in this way, for everyone knows the difficulty of obtaining results of a very high grade of accuracy by their aid. In this laboratory, the burette is only called into use when at least 99 per cent of the material has been weighed out, and then only a few c.c. of a very dilute solution are added to complete the quota. This is quite a different story. It is evident that nearly all the errors mentioned tend to make Winkler's result too high.

Some singular oversights appear also in the calculation of the results. For example, in one place Winkler compares 0·1662 grm. of nickel with 0·6079206 grm. of silver. The small amount of nickel was deposited in a large platinum dish, and its weight could certainly not have been determined more accurately than within 0·1 m.grm., hence at least three decimal places of the recorded weight of silver were superfluous, even if the volumetric solution could have been prepared with an error of only one part in six millions. It is perhaps well to mention also that his final results, varying in the case of cobalt from 59·5996 to 59·7480 (if O=15·96), are given as far as four decimal places.

While a review of this work is necessary in order to

explain why the results should be too high, perhaps one should not be severe in one's criticism of it, for Professor Winkler himself rejects it, as well as some later work on cobalt (*Zeit. Anorg. Chem.*, iv., 462), in his most recent contribution upon the subject (*Zeit. Anorg. Chem.*, xvii., 236). In this new paper he pins his faith to another series of determinations made in 1894, with a very ingenious method adopted after sundry fruitless attempts in other directions. It behoves us, then, to consider this later work with great care.

(1894, 1895, Winkler, *Zeit. Anorg. Chem.*, viii., 1291; Ni=58·85. It must be borne in mind, in referring to Winkler's papers, that he uses the old standard O=15·96. His values have all been translated into the more convenient notation, O=16·000, in this paper).

Evidently many of the errors which render the older investigation untrustworthy were eliminated from that of the subsequent year. The nickel was separated from the platinum dish and afterwards ignited in an atmosphere of hydrogen, and the solubility of argentic chloride does not enter into the question. On the other hand, the unfortunate use of volumetric operations and the misuse of figures remained, while to these were added other dangers not present in the older work. The ingenious procedure was as follows: pure nickel was acted upon by pure iodine, and the excess of iodine was determined by sodic thiosulphate. Many text-books upon volumetric analysis name the process of iodometry as one of the most accurate of titrimetric methods simply because the end point is an extremely sharp one. In reality, the lack of permanence of the necessary solutions render it distinctly unsuitable for very accurate work even under the best conditions. When the iodine must remain in solution for twenty-four hours after weighing and before titration, and when this circumstance is complicated by the presence of a metal capable of acting to a slight extent even upon pure water in the presence of air, one can hardly contend that the conditions are the best. The chance of side reactions seems to be too great to admit of infallibility in the results. One is surprised, indeed, that Winkler's results approach as near to those of Zimmermann as they do, and this close approach is evidence of great accuracy of manipulation on Winkler's part. In short, viewed from the standpoint of ordinary analytical experience, Winkler's last work is admirable, while from the standpoint of atomic weight research it is inadmissible. In justice to Professor Winkler it is only fair to add that he realises this fact himself (*Zeit. Anorg. Chem.*, xvii., 239). One need not dwell upon possible inaccuracies, however; for Winkler himself has furnished us with data for computing the error of his method. In a short paper he uses the same method for determining the atomic weight of iron, and finds for this quantity the value 56·174, if O=16·000 (*Zeit. Anorg. Chem.*, viii., 291). Now, according to the fairly consistent work of Berzelius, Erdmann and Marchand, Svanberg and Norlin, and Maumené, the atomic weight of iron cannot be far from 56·02; and there is no contradictory evidence of serious value.* Winkler's method, then, gave him a result 0·275 per cent† too high in the case of iron, and it is fair to conclude that the error could not have been far different in the case of nickel. Making the corresponding subtraction, Winkler's corrected result approaches astoundingly near to those obtained by Zimmermann and by us.‡

Winkler's corrected value	58·69
Zimmermann's value..	58·694
Richards and Cushman's value ..	58·706
Average	58·70

* Clarke's "Re-calculation," p. 289. The atomic weight of iron is now being further studied in this Laboratory.

† It is possible that a small part of this error is due to the omission of the reduction to the vacuum standard, which would affect the final value by about 0·01 per cent. This correction may have been applied, but there is no evidence of such application.

‡ Mr. Baxter first called our attention to this remarkable unanimity.

Owing to a slight uncertainty in the atomic weight of iron, as well as to the possibility that iron may behave somewhat differently from nickel in iodine solutions, this comparison is less significant than it seems to be; but certainly it does not militate *against* our value for the atomic weight of nickel. It is of interest to note that Clarke's mathematical method of selecting from among the older values led to the number 58·687.

Professor Winkler's sixth and last paper upon this subject appeared only last summer, after the work described in this paper had been completed (*Zeit. Anorg. Chem.*, xvii., 236). In it he kindly points out several possible flaws and omissions in our earlier paper. This criticism will be discussed at length in the next paper on cobalt.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, March 29th, 1899.

Professor Dewar, F.R.S., President, in the Chair.

Dr. E. W. Voelcker and Mr. W. P. Bloxam were appointed scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's Address.

The President, in beginning his Address, said that the past two years had been marked by change in the ranks of the active officers of the Society. Last year, Professor Thomson, who had been an Honorary Secretary since March, 1883, resigned office. His services to the Society had been beyond praise, not only from the amount of work actually done, of forethought and care expended, but also from the personal influence which enabled him to discharge the often delicate duties of his office without wounding the susceptibilities of those with whom he had to deal. Dr. Wynne who became Junior Secretary last year, had now resigned the post to take up the arduous duties of Editor of the Society's Journal. Dr. Thorpe, who had been Honorary Treasurer since 1889, vacated the office that day, the eminent services which he has rendered, not only to chemical science, but to the Society, recommending him to the Council for the highest honour the Society had to bestow. Dr. Tilden, who had served the Society twice as Vice-President, would succeed him as Treasurer, and Dr. Scott had been nominated to succeed Dr. Wynne as Secretary. The names of these gentlemen were familiar to the Society as those of persons in every way qualified to discharge the duties of their respective offices.

The Treasurer, as he might still for some minutes call him, would no doubt render them an account of his stewardship, but the duty was incumbent upon him of expressing their deep sense of the debt of gratitude owed him by the Society. During ten years of office, despite the magnificent undertakings of which Dr. Thorpe had been the mainstay, the investments of the Society had increased by one-half, and its income had risen from £4150 to £5286, while, largely owing to his vigilant care, the tendency to an increased expenditure had been kept down to normal proportions.

During his term of office he had had to provide the funds for some very considerable undertakings, chief amongst which were the alterations effected in the meeting room and the introduction of the electric light in 1892, the Society's Jubilee in 1891, and the drawing up of General Indexes to the Society's Journal and the Abstracts from 1873 to 1892. On the completion of this latter piece of work, which Dr. Thorpe would announce to the meeting, it seemed a fitting time to acknowledge the service which the publication of these volumes has

rendered to everyone interested in the science. They had been issued gratuitously to all Fellows who had received the Journal during the period they cover, provided that application was made for them before December, 1895.

Though the initiative in this issue had been taken by our illustrious colleague, the main burden of the preparation of the index had fallen on a lady, Mrs. Dougal, who edited the two volumes with zeal, energy, and intelligence. He (the President) would wish to bear testimony to her self-sacrificing devotion to this task, which had occupied upwards of five years. It had proved to be one of uncommon and unexpected difficulty. The annual indexing was found to have been done in an irregular and unsystematic way in the past, and much of the work which was understood to be ready to her hand had to be done over again. She had, both directly and indirectly, done the Society a great service—directly, by the compilation which she had executed, and indirectly, by leaving an example of thoroughness and accuracy to her successors. He had also to tender their thanks to the ladies who assisted her, and to Miss Neale, who had taken her place for a short time. The thanks of the Society were also due to the Index Committee, and more especially to Dr. Forster Morley, whose unwearied assistance and experience did much to solve the problems which were daily met with in the progress of the work.

The yearly indexes to the journals had of late shown a tendency to expansion. With a view to making them of more service, a staff of indexers, having a special knowledge of the various departments they undertook, had been engaged.

During the past year the Society was privileged to offer to six of its Past-Presidents its congratulations, and those of the whole scientific world, on the occasion of their completing fifty years' Fellowship of the Society. The Banquet at which they were entertained would long live in their memory. To quote the words of Friedel, "No finer phalanx of the Fathers of our Science exists in any country." The occasion was too recent for him to add anything to the sentiments then expressed. The event, however, was not without a melancholy side. As originally proposed, the foremost of this phalanx would have been their senior Past-President, the last surviving founder of the Society. He would not speak here at length of the services Lord Playfair had rendered to science, but fifty years' active work in the service of the Society required a more special mention. He became a Member of the Council in 1846, in 1850 he was elected a Vice-President, in 1857 he became President of the Society in succession to Professor Miller, and from 1859, for forty years, he remained Vice-President of the Society to which his experience and influence rendered signal service. His last appearance amongst them had been to propose him (Prof. Dewar) as President.

During the past two years the Society had lost by death thirty-six of its Fellows. Lord Playfair was the last survivor of the seventy-seven original members of our Society. In Mr. J. W. Rodger, the Society lost one of the most promising of the younger men of science and a member of its Council. Sir Thomas Dyke Acland had been a Fellow of the Society for over forty years, and though he had never taken an active part in the affairs of the Society, he had rendered great services to our science in its connection with agriculture. Sir Douglas Galton, whose recent loss they had to deplore, had been a Fellow of the Society for a quarter of a century. Mr. Newlands, whose "Law of octaves" has taken an imperishable place in the history of science, was in his fortieth year of membership, and had also served the Society as a Member of Council. His portrait now occupied a place on their walls.

Mr. Groves, who had been connected with the Journal since 1878, first as Sub-Editor, and, in 1884, as Editor in succession to Mr. Watts, resigned office that day. Only those who have been connected with similar publications could measure the full extent of the Society's indebtedness to him, but they could all join the Council in expressing their deep sense of, and thanks for, the important services he had rendered to the Society during those twenty-one years. They could only express the hope that his work for the Society and for science might be continued for many years to come.

Mr. Greenaway, who had for so many years occupied the important office of Sub-Editor, and worked so harmoniously with Mr. Groves, had elected to remain in that position. Dr. Wynne had succeeded Mr. Groves in the editorial chair and could be trusted to preserve that high level of excellence to which the Society's Journal had attained.

The number of papers read before the Society during the past two years was 274, of which 216 had since been published in full in the Society's *Transactions*, the remaining papers being preliminary notices of a more or less temporary character.

The meetings of the Society had been well attended, and the discussions fruitful of interest, but he could desire, in the best interests of the Society, that a larger proportion of the senior members could find it possible to be present.

During the past two years considerable attention had been given by the Council to the question of a suggested revision of the By-Laws. It has been found that no important modification can be made in these without the grant of a new charter, and it is thought that it is hardly worth while to introduce mere verbal changes which might, perhaps, make the meaning of the By-Laws more clear, but which, the council is legally advised, are unnecessary in view of the established practice of the Society.

The next matter of importance which would engage the attention of the Society would probably be the issue of a new catalogue to the Society's Library. Originally founded in 1850, it then consisted of about 270 volumes of journals, 60 miscellaneous volumes, and 100 pamphlets. Its first catalogue was issued in 1851, a second catalogue was prepared by Mr. Watts and issued early in 1861, a third catalogue, now grown from 28 to 112 pages, was issued in 1869, and a fourth, of 138 pages, in 1874. In 1886, a new catalogue, arranged according to subject-matter, was drawn up by Mr. Warington from Mr. Watts's notes, and issued to the Society. It extends to 327 pages, and has an author-index drawn up by Professor McLeod. The catalogue of 1886 contains entries of 5580 volumes of journals, 4223 books, and 1380 pamphlets. Since that time there have been added 3279 volumes of journals, 1361 books, and over 1600 pamphlets. The preparation and issue of this important work would necessarily involve some considerable time and expense to the Society.

One of the great needs of scientific workers is a ready means of acquainting themselves with the bearing and results of general scientific work. The publication of abstracts of particular branches of science is, generally speaking, nearly complete, but there is great overlapping and waste of energy. The suggestion has been made that some change analogous to that recently carried out by the German Chemical Society should be made in the publication of our own abstracts. All such proposals will have the fullest consideration of the Council, but it is clear that it would be unwise to ignore the grave consequences to the financial position of the Society which might result from any too precipitate change in the method of publication of the abstracts. Without entering more fully on this question, he might remark that there was still room for co-operation in this matter between the societies of this country.

They had been asked to co-operate with the American and the German Chemical Society in bringing about an International agreement upon the subject of Atomic Weights. The Council has appointed a Committee to consider the matter.

In the meantime, they had had the opportunity of co-

operating in the movements designed to honour the memory of two illustrious chemists, Kekulé and Davy; the former by joining in the International Memorial to his memory, the latter by contributing, in conjunction with the Royal Institution and the Royal Society, to a fund designed to restore and preserve the memorial raised over his grave.

The remainder of the Address was of a general and theoretical nature, dealing with recent advances in chemical research, principally in connection with low temperatures.

The numerical strength of the Society was as follows:—

Number of Fellows, March 31st, 1898		2140
since elected		132
reinstated by Council		3
		2275
Removed on account of non-payment of two annual subscriptions	15	
Withdrawn	12	
Deaths	18	
	—	45
Number of Fellows, March 31st, 1899		2230
Foreign Members		38

The following have died:—Sir T. J. Dyke Acland, W. R. Burnett, Michael Conroy, E. Rider Cook, Ramchandra Dutta, George Foord, Sir Douglas Galton, Jeremiah Head, J. G. Heywood, W. L. Hiepe, Charles Lowe, J. A. R. Newlands, Eugen Obach, Lord Playfair, Manning Prentice, H. W. Seely, Matthew Smith, Samuel Spencer.

The number of communications made to the Society during the year was 150.

One hundred and two papers were published in the *Transactions* for 1898, occupying 1047 pages, whereas in the preceding year 114 papers were published, occupying 1204 pages.

The following were the statistics relating to the Abstracts.

	Pages.	No. of Abstracts.
Part I.		
Organic Chemistry	720	1187
Part II.		
General and Physical Chemistry		344
Inorganic Chemistry		284
Mineralogical Chemistry		171
Physiological Chemistry		165
Chemistry of Vegetable Physiology and Agriculture		159
Analytical Chemistry		516
	660	1639
Total in Parts I. and II. ..	1380	2826

Seven hundred and twenty-seven volumes had been borrowed from the Library. The additions comprised 67 books, 285 volumes of periodicals, and 24 pamphlets.

Dr. Gladstone, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*.

Dr. Armstrong, F.R.S., seconded the motion, which was carried by acclamation.

The President having returned thanks,

Dr. Thorpe, F.R.S., the Treasurer, in giving an account of the balance sheet, which he laid before the Society, duly audited, said:—

The receipts had been:—By admission fees and subscriptions, £4064; by sale of Journal and advertisements, £740 15s.; and by dividends on invested capital, £428 2s. 1d. The expenses had been:—On account of the Journal, £3007 9s. 10d.; on account of the Proceedings, £287 6s. 10d.; on account of the General Index, £793 16s. 7d.; on account of the Library, £294 19s. 11d.; House expenses, £238 2s. 7d.; the total expenditure being £5415 6s. 8d. Grants amounting to £245 had been made to Fellows from the Research Fund during the year, and a sum of £1316 1s. had been invested in the purchase of £1400 India 2½ per cent Stock.

On laying down his office as Treasurer, to which he was elected in 1889, Dr. Thorpe hoped that it might not be uninteresting to the Fellows if he gave a brief account of the financial progress of the Society during the ten years of his stewardship.

In 1889, the total assets of the Society, excluding the Research Fund, were £12,221; in 1899 they are £17,289.

The total assets of the Research Fund in 1889 were £5464; in 1899 they are £7618.

The aggregate total assets are now £24,907, as against £17,686 in 1889.

In 1889, the total receipts from Fellows were £3402 in 1899 they were £4064, or an increase of 19½ per cent. The annual income from the sale of the Society's publications in 1889 amounted to £365; this year, including an outstanding item on account of advertisements, it is £760, or an increase of £108 per cent. This is due partly to the increased circulation of the Journal and partly to the increased price which can be obtained for it. The advertisements now bring in an income equivalent to about £2000 of funded property.

The total income of the Society from all sources in 1889 including the balances at the bank was £5824; at the close of the present financial year it has amounted to £7180.

It will be seen, therefore, that whilst the receipts from the Fellows have increased by 19½ per cent, the income of the Society has increased by 23·3 per cent, and the total assets, some of which may be counted upon to still further increase the annual income, have increased by 40·8 per cent.

But if it may be said of societies, as of individuals, that their riches consist, not in the abundance of their possessions, but in the fewness of their wants, it is the experience of the Treasurer that the Chemical Society is by no means a rich corporation, for its wants advance, almost *pari passu*, with its possessions. His successor would find that, however ingenious he may be in securing money, the Society, with equal or with even greater ingenuity, will find a method of relieving him of it.

He regretted to find that he had—he hastened to add, by direction of the Council—signed cheques for a greater amount than any one of his predecessors. During the ten years he had been in office, he had disbursed nearly £45,000 of the Society's money. In explanation of this, he might point out that the annual cost to the Society of its publications has steadily increased since 1889. In that year the expenses connected with its publications came to £2565; this year, in spite of a considerable saving in the printer's bills, and in spite of the draconian methods of the Publication Committee, its publications, excluding the Collective Index, have cost £3370.

The expenses on account of the Library also steadily increase. In 1889, £196 was spent in books, periodicals, and binding; this year, which has been somewhat below the average of the preceding years, the amount has been £246.

The House expenses in 1889 came to £184; this year they are £238.

The total expenditure in 1889 was £3430; this year it has been £5415.

As regards these disbursements, he might be pardoned, perhaps, for pointing out that none of his predecessors had been called upon to spend so large an amount of the Society's money in what might be termed extraordinary expenditure. To begin with, his immediate predecessor handed him over—and it was his only legacy—certain applications for increase of salary on the part of the Editorial staff, and he was good enough to urge that he

should deal with them liberally. The liberality has resulted in a difference of £1000 to the Society.

In 1891, the Society celebrated its Jubilee, at a cost, notwithstanding the generous assistance of the Goldsmiths' Company, of about £450. In the following year, the alteration of the meeting room and the installation of the electric light was taken in hand, at a cost of £1490.

Shortly afterwards, the Society was called upon to provide for the declining years of an old and faithful servant. There was no circumstance connected with his official career as the Treasurer of the Society which he recalled with greater pleasure than its action in regard to Mr. Josiah Hall's pension.

In the early part of 1894, the Society determined to print a Collective Index of its publications from 1873 to 1892. This has proved to be even a more formidable undertaking than was expected. It has occupied nearly five years in execution, and has cost some £1740. It is now happily completed, and the Society may congratulate itself upon possessing an adequate key to the great store of chemical knowledge which it has accumulated during twenty years.

The revision of the annual indexes necessitated by this great work has shown the absolute need for their more systematic preparation. This has led to the establishment of a special staff of indexers, at an annual cost to the Society of upwards of £60.

Another item of expenditure which had arisen during his tenure of office is connected with the lectures which are given in memory of the deceased Foreign Members. The Society has now a collection of eight of these Memorial Lectures, all of which have been given gratuitously by Fellows or friends on the invitation of the Council. Their publication has cost about £400. These lectures together constitute a most valuable record of contemporary chemical history, and it is hoped that, as the Council have directed, they may be issued in a separate volume, with the accompanying illustrations, before the end of the next financial year.

In their donations to funds connected with the illustrious names of Lavoisier, Davy, Stas, Kekulé, Cannizzaro, the Fellows have not been unmindful of their obligations to these great pioneers in chemical enquiry, nor have they been forgetful, as the gathering of last November showed, of their obligations to the pioneers in their own Society happily still amongst us.

The account-books of the Society show that what he had called the extraordinary expenditure which has been incurred during the last ten years is close upon £7000.

He thought, however, they would all feel that, in the enhanced position of their Society, in the greater comfort and convenience of their meeting-room, in the improvement and increased value of their publications, they had had an abundant return for this expenditure. Although but for it he might have been able to add a few more thousand pounds to their capital account. He hoped the Fellows would not hold him responsible for this omission, but look with a lenient eye upon the financial transgressions of what he sometimes felt himself to have been —a too compliant purse-bearer.

Mr. David Howard proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Mr. F. J. M. Page, and carried.

The Treasurer, in responding, proposed a vote of thanks to the auditors.

Prof. Hodgkinson seconded the motion, which was unanimously adopted, and acknowledged by Prof. Tilden on behalf of Dr. Horace Brown.

Dr. E. W. Voelcker proposed a vote of thanks to the Officers and Council.

Mr. H. B. Baker seconded the motion, which was unanimously adopted.

Prof. Dunstan, F.R.S., responded on behalf of the Council.

Prof. Thomson, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Dr. Messel, and carried.

Mr. Groves, F.R.S., responded.

The scrutators having presented their report to the President, he declared that the following had been duly elected :—

President—T. E. Thorpe, Ph.D., D.Sc., LL.D., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Sir E. Frankland, K.C.B., D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., V.P.R.S.; A. W. Williamson, LL.D., F.R.S.

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Secretaries—Wyndham R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—William A. Tilden, D.Sc., F.R.S.

Other Members of Council—H. Brereton Baker, M.A.; E. J. Bevan; Frank Clowes, D.Sc.; H. J. H. Fenton, M.A.; W. Gowland; C. T. Heycock, M.A., F.R.S.; D. Howard; Rudolph Messel, Ph.D.; G. T. Moody, D.Sc.; H. Forster Morley, M.A., D.Sc.; Arthur Smithells, B.Sc.; James Walker, D.Sc.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 13, March 27, 1899.

Preparation and Properties of Crystalline Calcium Phosphide.—Henri Moissan.—The reduction of tricalcic phosphate by carbon gives, under certain conditions, a crystalline phosphide of calcium, of a dark red colour and having the formula P_2Ca_3. The most curious reaction of this new compound is the facility with which it decomposes cold water, forming calcium hydrate and phosphoretted hydrogen. It may be remarked that a great number of binary compounds of calcium have this curious property of decomposing cold water and forming a hydrated oxide and a gaseous compound of hydrogen united with the other element of the binary compound. Calcium hydride decomposes cold water with evolution of hydrogen, calcium carbide with evolution of acetylene, whilst calcium nitride gives the same reaction with formation of ammonia.

Properties and Applications of Aluminium.—A. Ditte.—The author has continued his researches on aluminium, more especially with regard to certain alloys of aluminium used in objects of military equipment. In the various alloys examined, he finds the aluminium is attacked very easily, being protected, as in the unalloyed state, by thin layers of fatty matter, &c., which, on being decomposed by alkaline matter, again exposes the surface of the aluminium to the action of other reagents.

Decomposition of Carbonic Oxide in presence of Metallic Oxides.—O. Boudouard.—This paper gives an account of the continuation of the author's work on the decomposition of carbon monoxide by metallic oxides. He has now continued his researches up to a temperature

of 650°. He finds that the reaction of the decomposition of carbonic oxide is a function of the time, and it depends also on the quantity of metallic oxide present. The quantity of carbonic acid formed increases in a regular manner, but whilst at 445° the decomposition of the carbonic oxide is total, at 650° it is limited. Experiments made in the presence of oxide of cobalt show that the reaction stops when the gaseous mixture contains 61 per cent of CO_2 and 39 per cent of CO.

Decomposition of Carbonic Acid in the presence of Carbon.—O. Boudouard.—The author examines the reaction $CO_2+C=2CO$ from a quantitative point of view at various temperatures, the first series of experiments being made at 650°. Glass tubes are used, in which the carbon is placed; the tubes are then filled with carbon dioxide and sealed. They are now heated for lengths of time varying from eight minutes to twelve hours. The proportion of CO_2 and CO is then measured. The decomposition of the carbonic acid gas at this temperature is never total, but it is curious to remark that the limiting proportion is the same as that found in examining the decomposition of carbonic oxide (61 per cent CO_2 and 39 per cent CO).

Dissociation of Mercuric Oxide.—H. Pélabon.—The author has studied the dissociation of mercuric oxide by finding the state of equilibrium of a system consisting of oxide of mercury, oxygen, and liquid mercury when a fixed temperature is maintained for a sufficiently long time. In this case, the thermodynamical theory of dissociation indicates that the tension of the oxygen in the system is a function of the temperature only, and depends neither on the mass of oxide of mercury, nor on the mass of the mercury contained in the system, and the author's experiments verify this result between the temperatures 440° and 620°. In the case when the system under examination does not contain liquid mercury at the temperature of the experiment, the tension limit of the oxygen depends on the value of the vapour-tension of mercury. The author has examined the particular case when the oxygen and mercury vapour are mixed in equivalent proportions, and has determined for each value of the temperature the tension-limit of the oxygen. The numbers obtained allow of a verification of a consequence of the theory of dissociation, by showing that, in this case, the product of the pressure of the oxygen by the square of the vapour-pressure of mercury is a positive number, of which the value depends on the temperature only.

Action of Bis-diazoic Chlorides of Benzidine, Ortho-tolidine, and Dianisidine on Ethyl and Methyl Malonates.—G. Favrel.—In the author's first experiments he uses a method analogous to that by which he has already prepared dihydrazones of cyanacetic ethers and acetylacetone. He obtains, in the presence of an alkali, a reddish yellow precipitate insoluble in excess of alkali, which, after desiccation, easily decomposes on a very slight rise of temperature. By reason of its instability, the product cannot be obtained crystalline or analysed. Much better results are obtained when acetic solutions are used. Yellow crystals are then obtained, melting at 178—180°.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., May 23, 1898.

The Oxidation of *p*-Nitrotoluenesulphonic Acid.—A. G. Green and A. R. Wahl.—It has been suggested that the acids already described by the authors (dinitrodibenzyldisulphonic and dinitro-stilbene-disulphonic) were not really free acids, but the acid salts of sodium, and that the latter contained one molecule of oxygen less than it should. To decide this point definitely, the authors have determined by analysis the quantity of zinc necessary to reduce the disodic salt of dinitro-stilbene-disulphonic acid, and they found that the figures corresponded very closely with those required by the formula they proposed and still consider correct, viz., $C_{14}H_{10}N_2S_2O_{10}$.

A New Method of Preparing *a*-m-Xylylsulphamic Acid.—A Junghahn.—By heating the crystalline mass formed by passing dry sulphurous acid through *a*-m-xylidine, in a sealed tube for five hours at 170—180°, the author obtained, from 30 grms. of xylidine, about 10 grms. of a compound which appeared to be the xylidine salt of *a*-m-xylylsulphamic acid formed according to the equation—

$$4C_6H_3\overset{(CH_3)_2}{\underset{NH_2}{<}}+3SO_2=$$
$$=S+2\left(C_6H_3\overset{(CH_3)_2}{\underset{NH.SO_3H}{<}}.C_6H_3\overset{(CH_3)_2}{\underset{NH_2}{<}}\right)$$

Iodochloride of Phenyl.—F. Keppler.—Iodochloride of phenyl is decomposed at the end of two months in the dark, one month in diffused light and a few hours in direct light in a closed vessel forming *p*-chloro-iodobenzene, fusible at 55—56°. It can, however, be kept in an open exsiccator by taking certain precautions.

Action of Sulphochloride of Phosphorus on the Aqueous and Alkaline Solutions of the Phenols.—W. Autenrieth and O. Hildebrand.—Sulphochloride of phosphorus, $SPCl_3$, acts readily, and generally in the cold, on the monovalent phenols and their substitution products, in aqueous and alkaline solution. Substances are formed corresponding to the general formulæ $SP(OR)_3$, $SP(OR)_2Cl$, $SP(OR)Cl_2$, in which R represents an aromatic residue. These compounds are insoluble in alkalis and are deposited immediately during the reaction. Acids of the formula $SP(OR_2)OH$ are also formed, and are found in the aqueous solution in the state of sodic salts. Sulphochloride of phosphorus may be considered as a reagent for the monovalent phenols and their substitution products; by its aid we can introduce into their molecules the inorganic radicals $(SP)'''$, $(SPCl)''$, and $(SPCl_2)'$.

The Synthesis of a Phosphazine.—W. Autenrieth and O. Hildebrand.—The authors find that by heating together the monophenoxylised sulphodichloride of phosphorus and *o*-phenylenediamine, the reaction takes place in two phases. It is probable that in the first phase one atom of chlorine is eliminated from the dichloride at the same time as one atom of hydrogen is eliminated from one of the "amido" groups of the *o*-phenylenediamine to form chlorhydrate of diamine, and an intermediate product which has not yet been isolated. On then heating to 170° the formation of a nucleus takes place with the elimination of hydrogen:—

$$SP\begin{cases}OC_6H_5\\NH\\(ClH)NH\end{cases}>C_6H_4=HCl+PS\begin{cases}OC_6H_5\\NH\\NH\end{cases}>C_6H_4.$$

The *p*-thiophenoxylphenphosphazine thus obtained crystallises in alcohol in fine prisms, melting at 185°; they are almost insoluble in cold water, slightly so in warm water, and easily in alcohol, ether, &c.

Synthesis of Aromatic Aldehydes.—L. Gattermann.—Starting from the supposition that prussic acid or certain of its derivatives might exist in the tautomeric form C=NH, the author presumed that aromatic bodies might be added to it in the presence of chloride of aluminium, in the same manner as carbonic oxide. Research has confirmed this idea, and the author has prepared, by means of anisol, phenetol, and the cresol ethers, the corresponding aldehydes with almost quantitative returns.

Formation of Acetohydroquinone by means of Acetaldehyde and of Benzoquinone under the Influence of Sunlight.—H. Klinger and W. Koldenbach.—The authors have prepared acetohydroquinone,—

$$CH_3CO.C_6H_3(OH_2),$$

by submitting a mixture of benzoquinone and freshly distilled acetaldehyde in a sealed tube to the prolonged action of direct sunlight. This compound sublimes in long needles of a greenish yellow colour, melting at 202°; it is soluble in soda-lye, ammonia, or a solution of carbonate

of soda, giving an intensely yellow colour; acids re-precipitate it from these solutions. Its dibenzoate, $CH_3CO.C_6H_3(OCO.C_6H_5)_2$, prepared by means of chloride of benzoyle, crystallises in alcohol and benzene in prisms melting at 113°; the corresponding phenylhydrazone occurs in brilliant straw-coloured needles, fusible at 148°.

On some Perhaloïds.—A. Samtleben.—The author has examined the action of halogens on the tertiary amines of the benzene series, as well as on some acetonic cyclic bases. When bromine, iodine, or chloride of iodine is made to react on the free tertiary bases of the aromatic series, substitution products are formed; but if we cause them to react on the chlorhydrates, bromhydrates, or iodhydrates of the above-mentioned bases, coloured products of addition are generally formed. In nearly every case compounds are formed having the general formula $R.H.X-X_2$, in which R = a tertiary amine and X an atom of a halogen. The perhaloïds may be represented by the following formulæ.—$R.HCl.ClI$; $R.HBr.Br_2$; $R.HI.I_2$.

Ethyltriamidonaphthalene and its Acetyl Derivative.—O. Markfeldt.—The author has prepared ethenyltriamidonaphthalene by the reduction of dinitroacet-α-naphthalide by means of iron and hydrochloric acid, and has studied the nitric colouring-matters derived therefrom, of which some appear to be of interest The acetyl derivative was obtained by the usual method, starting with the chlorhydrate; its acetate crystallised in white flakes, fusible above 280°; it contains 3 molecules of acetic acid, two of which are in the form of acid of crystallisation.

$$C_{10}H_5\begin{cases}NH\\ N=C.CH_3\\ NH.C_2H_3O\end{cases}.CH_3COOH+2CH_3.COOH.$$

The acetyl base itself crystallses in silky needles, difficultly soluble in cold water, fusible above 280°, and containing 2 aqua. The author also describes the chlorhydrate of the acetylised derivative, the sulphate, nitrate, and picrate.

Indigo Oxime.—J. Thiele and R. H. Pickard.—When indigo is treated with an alkaline solution of hydroxylamine it dissolves very easily, giving a monoxime; but the dioxime cannot be obtained even with a large excess of hydroxylamine. This oxime crystallises in alcohol in violet-brown coppery needles, melting with decomposition at about 205°.

MISCELLANEOUS.

Thorium Nitrate.—This chemical has suffered an enormous fall in value during the past year. At the commencement of 1895 the nitrate was selling for 1800 m. to 1900 m. (£90 to £95) per kilo. To-day it can be obtained for 37 m. per kilo. This strikingly rapid fall in price is due, not to competition, but to a change in the raw material used and in the method of manufacture. In 1895 the costly Norwegian thorite was used, and to obtain 1 kilo. of thorium nitrate 800 m. to 900 m. had to be expended upon raw material. The monazite, which is now alone used at the starting-point of the manufacture, was not a marketable article in 1895. The production of thorium nitrate three years ago was also a mere fraction of that of the present day, and, as usual, the increased scale of manufacturing operations has tended to cheapen the cost per kilo. The present prices are, however, too low to render the manufacture, as carried on to-day, profitable.—*Chemist and Druggist.*

A New Indicator for Acidimetry and Alkalimetry.—Em. Riegler.—A solution of guaiacal in alkali, mixed with a solution of diazoparanitraniline, gives a coloured diazo-body of the formula $C_6H_4—NO_2—N=N—C_6H_3O.CH_3.OH$. This body, which is brown, is soluble in alcohol and insoluble in water. The indicator is obtained by dissolving 0·2 gr. of the above compound in 100 c.c. of alcohol. One or two drops of the solution give with alkalis a beautiful red coloration. The slightest excess of acid changes the colour to greenish yellow. The sensitiveness of this indicator is greater than that of phenolphthalein. To prepare the diazo-body, 1 grm. of guaiacol is dissolved in 50 c.c. of water to which has been added 30 c.c. of a 10 per cent solution, and into this a solution of diazonitraniline is introduced, prepared as follows:—1·25 grs. paranitraniline, 50 c.c. distilled water. and 4 c.c. concentrated hydrochloric acid are placed in a flask, which is warmed until solution is complete. 100 c.c. of cold water is then added, and, when the mixture is cool, 0·5 gr. sodium nitrite in about 30 c.c. of water. In mixing this solution with that of the guaiacol, a red liquid is obtained, from which the insoluble coloured body is precipitated by acidifying with strong sulphuric acid, added drop by drop. The precipitate is washed, and dried in a desiccator over sulphuric acid.—*Bulletin de la Société des Sciences de Bucarest, Roumania*, 1898, No. 6.

MEETINGS FOR THE WEEK.

MONDAY, 24th.—Society of Arts, 8 (Cantor Lectures). "Leather Manufacture," Prof H. R. Procter, F.I.C.
—— Society of Chemical Industry, 8.30. "The Relations of the Society to Chemical Engineering and to Industrial Research," by George Beilby.
TUESDAY, 25th.—Royal Institution, 3. "Zebras and Zebra Hybrids," by Prof. J. Cossar Ewart, M.D., F.R.S.
WEDNESDAY, 26th.—Society of Arts, 8. "Coal Supplies," by T. Forster Brown.
THURSDAY, 27th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, M.A., LL.D., F.R.S.
—— Society of Arts, 4.30. "Judicial Reform in Egypt," by Sir John Scott, K.C.M.G., D.C.L.
FRIDAY, 28th.—Royal Institution, 9. "Some Features of the Electric Induction Motor," by Prof. C. A. Carus Wilson, M.A., M.Inst.C.E.
SATURDAY, 29th.—Royal Institution, 3. "Machiavelli," by Louis Dyer, M.A.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,

BURLINGTON HOUSE, LONDON, W.

The NEXT ANNUAL MEETING of the ASSOCIATION will be held at DOVER, commencing on WEDNESDAY, SEPTEMBER 13, 1899.

PRESIDENT-ELECT:

Prof. MICHAEL FOSTER, M.D., D.C.L., LL.D., Sec.R.S.

Notice of Papers proposed to be read should be sent to the Office, Burlington House, before JULY 1.

Information about local arrangements may be obtained from the LOCAL SECRETARIES, Castle Hill House, Dover.

G. GRIFFITH, Assistant General Secretary.

MASON UNIVERSITY COLLEGE, BIRMINGHAM.

FACULTY OF SCIENCE.

RESEARCH SCHOLARSHIPS.

(Founded by the late T. AUBREY BOWEN, Esq, of Melbourne, Australia).

(*a*) Two BOWEN SCHOLARSHIPS in ENGINEERING, each of the value of about £96.
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(*c*) Three PRIESTLEY SCHOLARSHIPS in CHEMISTRY, each of the value of about £96.

The object of these Scholarships is to encourage higher work and research in Scientific Professional Engineering and in Chemical and Metallurgical Science.

Applications, supported by details of educational training, and references to former teachers and others, should be sent to the Registrar on or before the 1st June, 1899. The awards will be made in September next, and the Scholarships will be tenable during the Session 1899-1900.

Further particulars may be obtained on application to the REGISTRAR.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E, M.S.C.I.,

Fellow of the Chartered Institute of Patent Agents,

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2057.

IRON SEPARATIONS WITH ALKALINE SALTS.

First Paper.

By HARRY BREARLEY.

For the separation of iron from manganese, zinc, nickel, cobalt, and in some cases copper, the most commonly used reagents are alkaline acetates and phosphates in a more or less acetic acid solution. Occasionally, though less now than formerly, sulphates are also used.

Any proposed reagent must obviously form an insoluble compound with iron, either in the cold or by subsequent heating. In view of the fact that ferric solutions may be "neutralised"—*e.g.*, arranged so that a small fraction of the original solution of the salt holds most of the iron dissolved as hydrate, $Fe_2Cl_6.8Fe_2(HO)_6$—it is permissible to use reagents which form comparatively unstable compounds, and whose use for precipitating "unneutralised" solutions of ferric chloride is not satisfactory. The value of such a reagent is illustrated by a former paper, "Separations with Alkaline Chromates" (Chem. News, lxxviii., 14).

Some available reagents are alkaline acetates, phosphates, sulphates, chromates, tungstates, and molybdates. The object of these papers is to present the essential features of the commoner reagents, the principles on which they are based, and the limits within which they should be used. Chromates, molybdates, and tungstates, particularly the two latter, require more detailed treatment. At present their possibilities are unknown, and we cannot say what special features they may have; they have at least *the* essential property—they form insoluble compounds with iron.

The Separation as Acetate.

A former series of articles on "Separations with Alkaline Acetate" (Chem. News, vols. lxxv. and lxxvi.) makes it unnecessary to discuss here the merits and demerits of this very common reagent at any great length. I am induced to include it in this series for the sake of completeness, and to afford myself an opportunity of making known certain additional facts concerning its use.

The following experiments, amongst others, are the outcome of a criticism of the latter portion of the method of separating iron and nickel described in Arnold's "Steel Works Analysis," page 163. This method is typical of the misuse of alkaline acetates for the above purpose, and, unless such meaning is read into the words as they do not properly convey, it cannot give accurate results.

The source of error lies in the enormous excess of acetate used: this defect is supposed to be compensated for by adding the acetate *to the cold solution*, and then raising the mixture to boiling. This instruction originated with Wollcott Gibbs (Chem. News, xi., 102), and has been repeated and sworn by over and over again. Personally I have for some time had little respect for this cumbersome detail, having previously shown that other abuses of the acetate separation being avoided, the separation was as satisfactory with as without it. I have now to show that the advantage claimed for it is an unreal one,—that, in fact, it is a harmful as well as a troublesome modification.

I have chosen the separation of iron and nickel to illustrate the question generally, because that element is more difficult to separate than any of the other elements for which acetate is commonly used. The points elucidated should, however, be taken as applying with greater or less force to the separation of iron from manganese, zinc, cobalt, or copper.

Four grms. of iron along with 0·4 grm. of nickel were dissolved in hydrochloric and oxidised with nitric acid, partially neutralised, and divided into four equal portions. After dilution 10 c.c. of strong ammonium acetate was added, in drops and with vigorous shaking, to each at the indicated temperatures. The figures are grms. of nickel recovered. The series shows unmistakably that the addition of acetate to the cold solution is the very worst time at which it could be made.

Temperature.	Grms. Ni recovered.
Cold (16° C.)	0·0833
60° C.	0·0863
80° C.	0·0910
Boiling	0·0947

This result was anticipated, on the following grounds, some time before an opportunity occurred of testing the point experimentally.

A large excess of acetate always leads to an imperfect separation. This arises from the fact that—

1. The excess of acetate transforms the nickel as well as the iron salts into acetates.
2. *Along with* the decomposition of the ferric acetate the nickel is also partially decomposed.

A separation of iron and nickel is therefore influenced by two factors—the excess of alkaline acetate and the decomposing ferric acetate.

When the acetate is added to the cold solution both these factors exert their maximum influence. On adding acetate to the boiling solution the first portion of it precipitated the iron; when the remaining portion is added the conditions are changed: now the iron is present in suspension only, and its influence is greatly lessened.

This is an important point. Previous experiments have shown that the use of minimum acetate leads to the perfect separation of iron and nickel; but the excess which could be used without causing an imperfect separation has been represented as being very small. This is because, in the experiments made to test the matter, the acetate, for the sake of uniformity, was added to the cold solution.

The acetate separation, as we have previously described it, has been subject to the criticism—not a very serious one—of disallowing the free and easy use of the precipitant: this criticism is tempered somewhat, if it be understood that the acetate is to be added slowly to the boiling solution. By way of comparison the figures of column I. are reprinted from Chemical News (lxxvi., 224), under precisely such circumstances as were then arranged, except that the acetate was added to the boiling solution; we now obtain the figures of column II.

Dilute* am. acetate.	Per cent Ni recovered. I.	II.
10 c.c.	100	—
20 ,,	99·0	99·8
50 ,,	95·2	98·1
100 ,,	90·0	94·8

* 75 c.c. strong acetate made up to a litre.

It is pleasing to find that the most convenient conditions —addition of acetate to the hot solution—should be also the most desirable in point of exactness.

Two other points generally insisted on are that a separation increases in exactness as the iron decreases, nickel being constant, and similarly iron being constant, the separation is better for small than large amounts of nickel, assuming, of course, that the circumstances are otherwise the same so far as amount of acetate used, volume of solution, &c., are concerned.

The former of these two conclusions is by no means obvious if we bear in mind the *rationale* of an acetate separation. As a matter of fact the separation may be better or worse, or equally good.

Suppose our solutions of nickel containing varying amounts of iron are all completely neutralised, there will

be the greatest amount of iron existing as ferric chloride in those samples containing the most iron: this means that more ammonium acetate will be needed to convert it into $Fe_2(C_2H_3O_2)_6$, and (the same amount of acetate being added to each sample) consequently the excess of acetate, which alone is harmful, will be less. And again, in the hot solution the $Fe_2(C_2H_3O_2)_6$ is decomposed and free acetic acid is liberated. Both these changes are favourable to improving separations, and they may be made so great as to afford a better separation from two than from two-tenths grms. of iron.

Here, as before, the matter is most easily settled by arranging relatively imperfect separations through the use of large amounts of acetate. The experimental details are—Nickel 0·1 grm., varying iron, perfect neutralisation, 10 c.c. acetic acid each assay, volume of solution precipitated from about 500 c.c. and 10 c.c. strong* ammonium acetate added to the cold solution.

Iron added.	Ni recovered.
2 grms.	0·0932
1 grm.	0·0884
0·5 ,,	0·0897
0·2 ,,	0·0916
0·05 ,,	0·0954

The second conclusion, viz., that with increasing amounts of nickel, iron being constant, the separations are less exact, seems more likely to be generally true. The absolute amount of nickel lost may be greater where the amount of nickel present is greater. It has yet to be shown that the percentage loss varies in the same direction.

ELECTROLYTIC SEPARATION OF COPPER FROM MERCURY, AND OF COPPER FROM ARSENIC.

By N. REVAY.

I. *Separation of Copper from Mercury.*

A. *Precipitation in Acid Solution.*—Although Freudenburg claims to have separated mercury from copper in acid solution, the author has not succeded in obtaining satisfactory results by this method. The electrolysis was conducted with the greatest care, and strictly according to the conditions laid down by Freudenburg, but without success.

B. *Electrolysis of the Solution of Double Oxalates.*—This method is already known, and gives good results. It is therefore not necessary now to describe it.

C. *Electrolysis of the Solution of Double Cyanides.*—This method has given good results to Smith and Freudenburg; but Smith and Frankel were unable to effect a complete separation when the proportion of copper present was greater than 25 per cent. This is due to the fact that the difference of potential between mercury and the solution of its cyanide varies considerably with the concentration of the liquid. According to Werner and Bolton the polarisation is greater as the number of ions of mercury present is smaller. By using 0·5 to 0·6 grm. of crystallised sulphate of copper, and quantities of mercuric chloride varying from 0·25 to 1·0 grm., and adding 3 grms. of cyanide of potassium, the author has found the following proportions of mercury in the mercuric chloride:—1, 73·60; 2, 73·75; 3, 73·73; and 73·76; the theoretical proportion being 73·80 per cent. These results were obtained with an electromotive force of 1·8 to 1·9 volts, and the mercury obtained was perfectly free from copper,

II. *Separation of Copper from Arsenic.*

To effect this separation it is necessary to work under such conditions that the copper will be deposited on the cathode and the arsenic on the anode. The conditions are easily arranged when the arsenic exists in the solution in the state of an anion (as in arseniate of potassium, for example), and is not easily transformable into a compound in which it would play the part of a cathion. We can use an acid, ammoniacal, or cyanide solution, with an electromotive force of 1·6 to 1·8 volts. If the difference of potential is too high, the arsenic is partly precipitated at the cathode in the form of a grey powder, probably by reason of the reduction of the pentavalent arsenic to the trivalent form. This takes place specially when the trivalent arsenic is susceptible of forming a salt with the acid ion (in hydrochloric solution, for example). This transformation is less easy in nitric solution, and still less so in sulphuric solution. It is therefore preferable to work in sulphuric solution. Cyanogen has very little tendency to form a salt with arsenic; electrolysis can, therefore, be just as easily effected in a double cyanide solution. Good results have also been obtained in ammoniacal solution.—*Zeitschr. für Electrochemie*, iv., 329.

* By neutralising 0·880 ammonia with 33 per cent acetic acid.

THE ANALYSIS OF GLUE.

By RICHARD KISSLING.

Two new methods have recently been proposed for the analysis of glues. Stelling (*Chem. Zeit.*, 1896, xx., 461) recommends the estimation of the non-gluey material; Fels (*Chem. Zeit.*, 1897, xxi., 56) proposes estimating the viscosity of a solution of the glue.

I have made a number of experiments to determine the relative values of these two methods, and I propose to record briefly the results I have obtained.

Stelling's process consists of adding to a solution of glue (1 part of glue to 4 parts of water) alcohol at 96°, in small quantities at a time, while constantly stirring (we take 15 parts of glue and 60 parts of water, and make up to 250 c.c. with alcohol).

We then determine the proportion of non-gluey matter present, by evaporating down an aliquot part of the alcoholic solution, previously filtered, and weighing the residue. This process is thus based on the supposition that alcohol at about 72 per cent in volume leaves the glutine intact, while it dissolves the products of decomposition, considered as non-gluey material.

I should here remark that the products meant by the term "non-gluey" should not be considered as products of decomposition of the glutine; they are also found in the original solution of glue, before it has undergone any destructive process by evaporation. I would also remark that the supposition that alcohol at 72 per cent is best for separating the glutine from the products of decomposition does not rest on any theoretical considerations, and if we proceed exactly according to Stelling's instructions this separation does not even take place.

Glutine is not entirely insoluble in alcohol at 72 per cent, inasmuch as, on evaporating down the filtered alcoholic solution, we obtain a residue consisting principally of glutine, and possessing a strong adhesive power, almost equal to that of the original glue employed.

Nevertheless it cannot be denied that Stelling's process has a certain value—very small, it is true—for the valuation of glues; above all when we have to deal with products of superior quality, products containing substances soluble in alcohol, in quantities much smaller than are present in ordinary glues.

Fels's method—that is, the determination of the viscosity—can also give very useful indications, but here again there are certain reservations which must be made. The viscosity is determined at 25° with an Engler viscosimeter. I claim to have discovered that solutions of glue undergo—after a more or less prolonged time of standing—modifications from the point of view of fluidity. In this way, a freshly prepared solution had a viscosity of 9·0°,

but after standing for twenty-four hours it had assumed a gelatinous consistency. Another solution underwent the following modifications:—Its degree of viscosity was 3·7 after two hours, 4·8 after twenty-four hours, and 5·4 after forty-eight hours.

I would here recall that the process I described (*Chem. Zeit.*, 1893, xvii., 726), some years ago now, while being somewhat more complicated than the above, merits more confidence in judging the value of a glue. This process consisted in measuring the consistence of the jelly formed by 100 grms. of glue and 300 grms. of water.

The question of determining whether a given glue is good or bad, is one which is not easy to decide, unless we have to deal with a product that is altogether inferior. In the greater number of cases we simply endeavour to decide whether the glue is suitable for such and such a purpose.

As far as the adhesive power is concerned I have shown, by numerous experiments, that, from this special point of view, the glue from bones—which is of a decidedly inferior quality—is quite as good as that made from skin, which is of a superior quality. It is quite another matter in so far as the consistency of the jelly is concerned. The researches which I have carried out in this direction lead me to the conclusion that the jelly made from glues from skin is generally firmer than the jelly derived from glues from bone.

In the examination of a glue it must not be forgotten to notice the smell; this characteristic may give very useful indications as to the resistance of the product, and its tendency, or not, towards putrefaction; with regard to the above, skin glues are much better than those made from bone. Finally, the proportion of acid present in a glue is a matter of capital importance for certain purposes for which it is required. The method I have proposed (*Chem. Zeit.*, 1897, p. 691, and 1892, p. 1316) for the estimation of free and combined sulphurous acid, has once more enabled me to satisfy myself that glues from skin are superior to glues from bone. The determination of the water, ash, and fatty matters gives less important indications.—*Chemiker Zeitung*, 1898, p. 171.

THE ESTIMATION OF MANGANESE; ELECTROLYTIC SEPARATION OF MANGANESE AND IRON.

By F. KOEPPEL.

THE author has devised a method enabling him at the same time to precipitate the manganese in the state of peroxide as a coherent powder, and to prevent the transformation of this peroxide into saline oxide by calcination in a platinum crucible. It is, of course, known that the platinum is strongly attacked in this operation.

The following is the method:—

The manganese salt is dissolved in 150 c.c. of water, and acetone is added. The solution is kept at a temperature of 50—55° C., and electrolysed with a current of 4 to 4·25 vols, and 0·7 to 1·2 ampères; care must be taken to add water to replace that which is gradually lost by evaporation. At the end of from two to five and a half hours, according to the proportion of acetone present (1·5 to 10 grms.), the operation is terminated; the peroxide of manganese is washed by means of a syphon, without interrupting the current; the electrode is dried at 150° to 180° C., and weighed.

The method for the electrolytic separation of manganese and iron, devised by the author, is sufficiently exact for commercial wants. In the presence of a great excess of pyrophosphate of soda, and a few drops of phosphoric acid, a solution of sulphate of iron and sulphate of manganese gives by electrolysis a deposit of metallic iron. A very small quantity of manganese is precipitated in the form either of binoxide or sesquioxide. The method is as follows:—

The solution of the mixed sulphates is poured, while stirring, into a boiling solution of 12 grms. of pyrophosphate of soda. When the solution has become perfectly clear we add 3 or 4 drops of phosphoric acid. If a slight cloudiness occurs, it suffices to add a slight excess of pyrophosphate of soda. The solution—which should be about 230 to 250 c.c. in volume, and have a decidedly alkaline reaction—is kept at a temperature of from 30° to 40° C., and electrolysed with a current of 1·8 to 2·5 ampères. The iron is completely precipitated in eight or nine hours. The deposit is washed with absolute alcohol, without interrupting the current, and the electrode is weighed after having been dried at a low temperature.—*Zeits. f. Anorg. Chem.*, xvi., p. 268.

SIXTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1898.*

By F. W. CLARKE.

DURING the year 1898, there has been an increased activity in the determination of atomic weights, and a considerable number of investigations have been published. The importance of the subject is also indicated by the fact that the German Chemical Society has appointed a strong committee to report annually upon atomic weights; and its action for the current year is stated further on. The new data are as follows:—

Oxygen.

Keiser (*Am. Chem. Journ.*, xx., 733) has effected the complete synthesis of water by a new method, in which the hydrogen held by palladium, the oxygen, and the water produced are all determined by successive weighings in one and the same apparatus. For details of construction, &c., the original memoir must be consulted. The data for four experiments are as follows:—

Weight H.	Weight O.	Sum H+O.	Weight H_2O.
0·27549	2·18249	2·45798	2·45975
0·27936	2·21896	2·49832	2·49923
0·27091	2·15077	2·42168	2·42355
0·26845	2·13270	2·40115	2·40269

From columns first and second, the ratio H : O can be computed, while the first and fourth give the ratio H : H_2O.

Ratio H : O.	Ratio H : H_2O.
7·922	8·929
7·943	8·946
7·939	8·946
7·944	8·950
Mean .. 7·937	Mean .. 8·943

From ratio H : O .. .. O = 15·874
„ H : H_2O .. .. O = 15·886

Mean .. .. 15·880

This value is very near that obtained by Morley, 15·879; and has corroborative value. Its great merit is in the directness of the determination, and in the avoidance of complicated or troublesome corrections.

Nitrogen.

The equivalent of cyanogen has been determined by Dean (CHEM. NEWS, lxxviii., 261, November 25, 1898); but as yet only an abstract of his work has appeared. Silver cyanide was dissolved in nitric acid, and titrated

* *Journal of the American Chemical Society*, xxi., No. 2,

by Stas's method with potassium bromide. The data give CN = 26·065; whence, if C = 12·01, N = 14·055.

Boron.

Armitage (Chem. News, lxxviii., 78: a paper read before the Chemical Society; not yet printed in full) has re-determined the atomic weight of boron by two methods. First, by determination of the percentage of water in borax, which had been washed with alcohol and ether successively, and then dried for six hours in a vacuum. The mean of six experiments gave—

B = 10·959.

Secondly, by the method of Rimbach. Fused borax was dissolved in water and titrated wiih dilute sulphuric acid. The mean of two experiments gave—

B = 10·928.

The abstract published gives no details of individual determinations, and neglects to state what values were assigned to the other atomic weights involved in the calculations, except that O = 16. The communication was discussed, in the main unfavourably, by Veley, Groves, Scott, and Dewar.

Armitage's paper called forth also a brief note from Leonard (Chem. News, lxxvii., 104), who refers to experiments of his own upon the dehydration of borax. He states that soda and boric acid are both volatilised when borax is intensely ignited, and that the composition of the residue is not constant. From this he concludes that the use of borax for determinations of atomic weight is liable to be attended by serious errors.

Zinc.

In the atomic weight determinations made some years ago by Morse and Burton, metallic zinc was converted into oxide, and in that way the ratio between metal and oxygen was measured. Later, Richards and Rogers showed that zinc oxide, prepared as Morse and Burton had prepared it, namely, by conversion of the metal into nitrate and subsequent ignition, always retained occluded gases, and in distinctly weighable quantities.

The research is now completed by the labours of Morse and Arbuckle (*Am. Chem. Journ.*, xx., 195, March, 1898), who have repeated the determinations made by Morse and Burton, with measurements of the occluded gases, and correction for them. In each experiment the gas, which consisted of oxygen and nitrogen, was analysed; and the corrections applied assume the litre weights to be, under standard conditions at latitude 45° and sea-level, 1·42923 grms. for oxygen and 1·25461 for nitrogen. The volumes are given in cubic centimetres.

Weight Zn.	Weight ZnO.	Volume gas.	Per cent O.	Atomic weight Zn.
1·19573	1·48860	0·468	26·28	65·459
1·03381	1·28707	0·402	18·14	65·445
1·06519	1·32599	0·342	18·42	65·459
1·05802	1·31711	0·312	18·58	65·440
1·26618	1·57619	0·521	13·82	65·489
1·03783	1·29198	0·408	35·28	65·475
1·08655	1·35276	0·412	19·55	65·437
1·11364	1·38647	0·456	18·62	65·447
			Mean..	65·457

O = 16. Vacuum weights are given. Without correction for occluded gases, Zn = 65·328, as against the earlier determination of Zn = 65·27. The new determinations agree closely with those of Richards and Rogers, who found Zn = 65·499, and of Richards alone, who found Zn = 65·404. The value assigned to zinc in the table of the Committee is 65·41, as published a year ago.

Cadmium.

In the case of cadmium the same uncertainty existed as in the case of zinc. Morse and Jones had determined the atomic weight by conversion of the metal into the oxide, in that way finding Cd = 112·06. Morse and Arbuckle (*Am. Chem. Journ.*, xx., 536, July, 1898) have repeated the investigation, this time with search for occluded gases in the oxide, and now give a new series of data, with corrections applied. In all essential features the research is parallel to that upon zinc, which had just been noted; and the results obtained are given in the subjoined table. The weights are reduced to a vacuum, and O = 16.

Weight Cd.	Weight CdO.	Volume of gas.	Per cent O.	Atomic weight Cd.
1·93188	2·20764	0·574	21·25	112·392
1·67935	1·91910	0·480	25·16	112·365
1·48430	1·69620	0·441	19·95	112·376
1·36486	1·55972	0·402	18·33	112·368
1·50295	1·71744	0·419	21·95	112·394
1·43804	1·64330	0·431	18·56	112·395
1·44041	1·64604	0·406	20·93	112·365
1·45938	1·66771	0·421	21·85	112·375
1·40379	1 60420	0·390	19·50	112·359
			Mean..	112·377

The uncorrected weighings give Cd = 112·084. Bucher, working with cadmium chloride and cadmium bromide, found the mean values 112·39 and 112·38, and the analysis of cadmium sulphate gave 112·36. These results accord fairly well with the determinations made by Dumas and by Huntington, but not with those of Hardin. The weight of evidence, however, now seems to be with the higher value, which may, with much probability, be adopted.

Cobalt and Nickel.

The paper by Winkler (*Zeit. Anorg. Chem.*, xvii., 236, June 25, 1898) upon these metals is merely a criticism of the determinations by Richards and Baxter and Richards and Cushman, which were noticed in the Committee Report for 1897. No new determinations are offered. Winkler suggests that the bromides prepared by Richards and his associates, which were sublimed in porcelain tubes, might have acted upon the glaze of the latter, and so have acquired impurities. He also suggests that perhaps the bromide might have retained an excess of hydrobromic acid, and he points out possible danger in the use of the Gooch crucible, in which the silver bromide was collected.

Selenium.

The atomic weight of selenium has been re-determined by Lenher (*Journ. Am. Chem. Soc.*, xx., 555, August, 1898), in the laboratory of the University of Pennsylvania. First, silver selenite was heated in a stream of gaseous hydrochloric acid, giving silver chloride, the latter being quite free from selenium. Three experiments gave as follows:—

Weight Ag_2SeO_3.	Weight AgCl.	Atomic weight Se.
0·98992	0·82715	79·326
1·59912	1·33600	79·373
2·70573	2·26087	79·320
	Mean	79·339

In a second series of eight experiments the silver chloride, after weighing, was reduced to metal in a stream of hydrogen. Thus the ratio between silver selenite and silver was measured. The weighings were as follows:—

Weight Ag_2SeO_3.	Weight AgCl.	Weight Ag.
0·26204	0·21897	0·16480
0·58078	0·48522	0·36534
0·70614	0·58999	0·44417
0·80811	0·67532	0·50821
0·98396	0·82232	0·61882
1·29685	1·08350	0·81562
1·63103	1·36288	1·02588
2·00162	1·67234	1·25884

Hence, for the atomic weight of selenium we have—

Ag_2SeO_3 : AgCl.	As_2SeO_3 : Ag.
79·299	79·356
79·371	79·280
79·350	79·301
79·282	79·369
79·263	79·358
79·361	79·277
79·316	79·320
79·358	79·357
Mean .. 79·325	Mean .. 79·329

Still another set of determinations was based upon analyses of ammonium bromoselenate, Am_2SeBr_6. This salt was reduced by hydroxylamine hydrochloride, and the precipitated selenium was weighed in a Gooch crucible. The results are subjoined:—

Weight Am_2SeBr_6.	Weight Se.	Atomic weight Se.
1·00059	0·13324	79·243
1·50153	0·20022	79·367
2·00059	0·26649	79·273
2·00126	0·26657	79·269
3·00125	0·39958	79·226
4·00216	0·53346	79·333
5·00218	0·66656	79·306
5·03001	0·66998	79·267
Mean		79·285

General mean of all twenty-seven determinations—

Se = 79·314.

The antecedent values are O=16, H=1·008, N=14·04, Ag=107·92, Br=79·95, Cl=35·45. All weights were reduced to a vacuum.

The result obtained is near that found by Dumas, but considerably higher than that given by Ekman and Pettersson. The reason for this disaccordance is yet to be found. In the table at the end of this paper the value assigned to selenium is the mean of Lenher's determination, and the value given in the Report of last year, namely, when O=16,—

Se = 79·17.

Neither the new nor the old determinations can be yet adopted to the exclusion of the other, and the mean value is the safest for present use.

Tellurium.

Metzner (*Ann. Chim. Phys.*, [7], xv., 272, October, 1898) has employed two methods for determining the atomic weight of this element. First, by synthesis of the sulphate, Te_2SO_7, which is perfectly stable at 440°. The tellurium which served as the starting-point was prepared by dissociation of hydrogen telluride, and was crystallised in beautiful needles. By solution in sulphuric acid, evaporation to dryness, and calcination at temperatures not over 440°, the sulphate was produced. The weights given are probably m.grms.

Weight Te.	Weight sulphate.	Atomic weight Te.
790·2	1235·0	127·9
414·3	647·5	128·0
1098·3	1717·0	127·8

Metzner's second method consisted in reducing tellurium dioxide by carbon monoxide in presence of metallic silver. The latter prevents the volatilisation of tellurium.

Weight TeO_2.	Loss of weight.	Atomic weight Te.
743·2	118·8	127·8
1106·7	221·3	128·0
988·5	197·0	128·24
1312·5	263·0	127·75

Metzner adopts 127·9 as the final result of his investigation. Apparently his weights were not reduced to a vacuum, and he neglects to state what value he assumed for the atomic weight of sulphur. O=16 was evidently the basis of his calculations.

The work of Metzner called forth two theoretical papers by Wilde (*Comptes Rendus*, cxxvii., 613, 616), who holds that the experiments show that the true value for tellurium is 128. In his second paper he discusses the positions of tellurium and iodine in the periodic system. As both communications are purely critical in character, and contain no new data, they need no further notice here.

Still another set of determinations relative to tellurium is due to Heberlein ("Beitrage zur Kenntnis des Tellur's," Doctoral Dissertation, Strassburg, 1898). First, telluric acid was dissolved in hydrochloric acid, and the liberated chlorine was distilled off into a dilute solution of potassium iodide. In the latter iodine was set free, and was titrated with a decinormal solution of sodium thiosulphate. The values found for Te, with O = 16 and H = 1·008, are—

127·16
127·28
127·32
127·35
127·09
Mean .. 127·24

Secondly, telluric acid was transformed into tellurium dioxide, by heating with proper precautions to avoid loss.

Weight $H_2TeO_4.2H_2O$.	Loss of weight.	Atomic weight Te.
1·35236	0·41431	126·60
1·76859	0·54122	126·84
Mean		126·72

Thirdly, tellurium dioxide was reduced to tellurium by means of hydrogen in presence of metallic silver.

Weight TeO_2.	Loss of weight.	Atomic weight Te.
1·35908	0·37353	126·99
1·94038	0·39050	127·00
Mean		126·995

The mean of all three series is Te=126·985.

It will be seen that some of these values range below, and others above, the atomic weight of iodine. Heberlein regards the higher figures as too high, and the lower as probably too low, the mean of all being most nearly correct. The main question, the position of tellurium in the periodic system, he considers experimentally unsettled, but favours the opinion that more critical determinations will place it below iodine and in the sulphur-selenium group. The value which he has actually found is only a trifle higher than that of iodine, and better determinations may well reduce it to the necessary amount.

Thorium.

Brauner's work upon the atomic weight of thorium (Chem. News, lxxvii., 160, April 7, 1898) has as yet appeared only in abstract. The determinations were made with the normal oxalate, in which thorium dioxide was estimated by heating, and the C_2O_3 was measured by titration with potassium permanganate. The values found for thorium with O=16 were—

232·50	232·33
232·46	232·50
232·45	232·44
232·31	232·35

In mean, Th=232·42.

Zirconium.

Venable (*Journ. Am. Chem. Soc.*, xx., 119, Feb., 1898), in order to determine the atomic weight of this element, has availed himself of the oxychloride, $ZrOCl_2.3H_2O$. This compound can be crystallised from strong hydro-

chloric acid, and dried in a current of gaseous hydrochloric acid at 100—125° without loss of its water. When dissolved in water in a platinum crucible, evaporated to dryness, and strongly ignited, pure zirconia, free from chlorine, remains. The ratio $ZrOCl_2.3H_2O : ZrO_2$ is thus determined, and from it the atomic weight of the metal is calculable. The results of ten experiments are given by Venable as follows:—

Weight $ZrOCl_2.3H_2O$.	Weight of ZrO_2.	Ratio.
5·25762	2·78450	52·961
3·53994	1·87550	52·981
3·25036	1·72435	53·051
1·52245	0·80708	53·012
1·98802	1·58274	52·969
2·11371	1·11920	52·949
2·38139	1·26161	52·978
1·90285	1·00958	53·055
2·61847	1·38658	52·954
1·07347	0·56840	52·951
26·64828	14·11953	52·986

Hence if O=16, H=1·008, and Cl=35·45, the atomic weight of zirconium becomes—

90·78 in mean,
91·12 maximum,
90·61 minimum.

As further results are promised, this investigation is to be regarded as a preliminary research rather than as a final determination.

Cerium.

Brauner's paper upon the compound nature of cerium (CHEM. NEWS, lxxvii., 160, April 7, 1898) has also only appeared in abstract. By a series of fractionations oxides were obtained giving atomic weights ranging from 140·25 down to 130·70. As the atomic weight decreases, the colour of the oxide changes from white to reddish-brown orange. Brauner infers that cerium is accompanied by another metal of atomic weight about 110. Yttrium was looked for in the lower fractions, but not found; nor were there any lines in the spark spectra other than those of cerium. The supposed new element, like gadolinium, may have no characteristic spectrum.

(To be continued).

ON THE SOLUBILITY OF ARGENTIC BROMIDE AND CHLORIDE IN SOLUTIONS OF SODIC THIOSULPHATE.

By THEODORE WILLIAM RICHARDS
and
HENRY BURNELL FABER.

IN the course of a series of experiments having a practical end as their chief aim, several determinations of the solubility of argentic halides in solutions of sodic thiosulphate were made. Since the data concerning this reaction are none too plentiful, it seems worth while to record briefly our incomplete work upon the subject.

The method of procedure was extremely simple. Solutions of sodic thiosulphate of known strength, made by dissolving weighed amounts of pure re-crystallised material in water, were agitated for varying lengths of time in test-tubes at a fixed temperature with an excess of argentic salt. The bromide had been freed from chloride by long-continued digestion with potassic bromide, and both argentic halides had been carefully washed, dried, and powdered. At the end of the allotted times, the agitator was stopped, the heavy precipitates were allowed to settle, and two portions were taken from each perfectly clear supernatant liquid by means of an accurate 5·00 c.c. pipette. The silver in these portions was now precipitated by sulphuretted hydrogen and collected on a Gooch crucible. Subsequently, the mixed precipitate and asbestos were treated with nitric acid in excess, the nitrous fumes were expelled, and the silver in the mixture was determined by Volhard's method.

The agitator, based upon the apparatus of Noyes (*Zeit. Phys. Chem.*, ix., 606; also Schröder, *Ibid.*, xi., 454), consisted simply of a rotating rod with a number of flat strips of brass soldered at right-angles to its axis. The rubber stoppered test-tubes were strapped to the brass strips by means of rubber bands, and the whole was immersed in a large Ostwald thermostat. A portion of the water of the thermostat was drawn off when it was desired to remove the solutions, so that the mouths of the test-tubes might be uncovered, and of course the projecting mouths were carefully dried. A spring curtain-rod supporter, easily obtained in New England, formed a very convenient support for the rotating rod when soldered to the sides of the thermostat. The results with the second solution showed that four hours' agitation was enough to insure saturation. No claim of great accuracy is made for the figures—indeed, the variations among them show their crudity—but they more than sufficed for our purpose, and are trustworthy enough to form an adequate basis for the remarks which follow.

The Solubility of Argentic Bromide in Solutions of Sodic Thiosulphate.

Temperature = 35°.

	Cryst. sodic thiosulphate in litre. Grms.	Weight of silver found in 5·00 c.c. solution. Grm.	Time of agitation.	Weight of AgBr corresponding to each grm. of thiosulphate. Grm.	AgBr corresponding to $Na_2S_2O_3$. Molecule.
1.	100	0·110	4 hours	0·376	0·496
2.		0·108			
3.		0·106			
4.		0·109			
		0·108			
5.	200	0·228	4 hours	0·390	0·515
6.		0·224			
7.		0·225			
8.		0·225			
9.		0·226	16 hours		
10.		0·223			
11.		0·220			
12.		0·223			
		0·224			
13.	300	0·339	4 hours	0·397	0·524
14.		0·340			
15.		0·347			
16.		0·341			
17.		0·344			
18.		0·337			
19.		0·337			
		0·341			
20.	500	0·613	4 hours	0·427	0·564
21.		0·611			
22.		0·611			
23.		0·619			
		0·613			

It is thus evident that the quantity of argentic bromide increases more rapidly than the quantity of the thiosulphate. In this respect the behaviour of the bromide resembles that of the chloride, as observed by Stetefeldt ("The Lixiviation of Silver Ores," Craz and Gerlach, Freiberg, Saxony). Hence, simply judging from the solubility, one has a right to infer that the solubility concerns itself with the undissociated part of the sodic salt, for this

is the part whose proportion increases when the concentration is increased.

The nature of the equilibrium is obviously so complex that the molecular ratios could not be expected to consist of simple whole numbers. Neither could the solubilities of the two halides be expected to conform to one another. In order to test this point, the solubility of argentic chloride in a solution of sodic thiosulphate containing 200 grms. of the crystallised salt to the litre was determined. Four parallel analyses of 5·00 c.c. of the solution saturated at 35° yielded respectively 0·344, 0·341, 0·342, and 0·341 grm. of silver, or on the average, 0·454 grm. of argentic chloride per grm. of sodic thiosulphate. (Russell found 0·400 and 0·485 by two different methods; the first was evidently not saturated, the second supersaturated; Stetefeldt, pp. 19, 20). Thus, the molecular ratio was in this case 1 : 0·78 instead of 1 : 0·52 as in the case of the bromide. The difference is undoubtedly due to the different solubilities of the argentic halides in water, which of course must be factors in the complex equilibrium.

It is well known that from these solutions two well-marked double salts (Herschel, *Edin. Phil. Journ.*, 1819, i., 26 and 398; also Lenz, *Liebig's Ann. Chem.*, 1841, xl., 94)—or, more probably, complex salts—may be obtained by crystallisation; but, of course, this fact does not show that these salts exist in the solution. As Barth (*Zeit. Phys. Chem.*, 1892, ix., 217) has pointed out, however, the inability of the solution to give the ordinary reactions of silver shows that a complex ion must be formed. More light might obviously be obtained from observations on the freezing- and boiling-points, as well as of electrolytic conductivities; indeed, Barth made an interesting beginning in this direction, and obtained evidence of the existence of a trivalent acid ion in the solution.

We proceeded in a somewhat different manner. Instead of studying the behaviour of the pure double salt, we observed the change in the freezing-point caused by the addition of argentic bromide to solutions of sodic thiosulphate. In one trial, the addition of 0·8 grm. of argentic bromide to 26 grms. of a 0·54 mole-solution* of sodic thiosulphate *raised* its freezing-point 0·08°, while in another trial the addition of 0·25 grm. of argentic bromide to 19 grms. of a 0·4 mole-solution raised its freezing-point 0·03°. Further additions in both cases produced no further rise, although much more argentic bromide dissolved; indeed, in the first case a slight fall was subsequently observed.

According to modern hypotheses, such a rise in the freezing-point can be produced only by the diminution of the number of active particles present. In the present case, the addition of another salt with different ions must, as usual, increase rather than diminish the dissociation of the sodic thiosulphate molecule; hence, it could have diminished the number of active particles only by causing some of the undissociated material to condense into a complex structure, in which the silver is combined. Thus, further evidence of the plausibility of Barth's conclusion as to the existence of a complex ion is afforded. The fact that upon the further addition of argentic bromide, no further rise is produced may be accounted for by the possible concomitant formation of another complex group, containing more silver—a reaction which might involve an increase in the number of active particles. The substances corresponding to these stages may well be the salts $Ag_2S_2O_3.2Na_2S_2O_3.2H_2O$ and $2Ag_2S_2O_3.2Na_2S_2O_3.2H_2O$, which are actually known in the solid state. The double formula is assigned to the second salt simply in order to show at a glance that it contains more silver than the first. It is more likely that this second salt possesses a simpler formula, and that its partial formation, even in the beginning, prevents the rise in the freezing-point from being as great as it would be if influenced by the formation of ions of the first salt alone.

In the course of the work, the depression of the freezing-point of water caused by the addition of sodic thiosulphate was also observed, as follows:—

Grm.-mol. in litre.	Depression of freezing-point.
0·202	0·855°
0·404	1·590°
0·535	1·980°

In brief, this paper contains data concerning the solubility of argentic bromide and chloride in solutions of sodic thiosulphate, cognate results upon the freezing-points of the solutions, and a few remarks upon the probable nature of the complex substances formed. The subject is one of great interest, but the time at our disposal, as well as the inherent obscurity of the equilibria of concentrated mixed solutions, does not suffice to present a more complete view of the details of the reaction.—*American Chemical Journal*, xxi., No. 1.

* That is, a solution containing 0·54 × 248·3 grms. of sodic thiosulphate in a litre. Such a solution would be called by some a 0·54 normal solution; but it seems to us that this nomenclature is an unfortunate one, and that the term "normal solution" should be reserved for the *equivalent* solutions so useful in volumetric analysis.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

Second Paper.—The Determination of the Cobalt in Cobaltous Bromide.

By THEODORE WILLIAM RICHARDS
and
GREGORY PAUL BAXTER.

In a recent paper upon the atomic weight of cobalt (*Proc. Amer. Acad.*, xxxiii., p. 115) we began the analysis of cobaltous bromide by the determination of its bromine, with results which seemed to show that the atomic weight of cobalt is very nearly 58·99 (O = 16). Although very great care was taken in purifying the cobaltous bromide used in this work, it was never certain that during the sublimation of the bromide in the porcelain tubes small amounts of impurity had not crept in. The situation here was exactly the same as in the research upon nickel, carried on at the same time in this Laboratory (see *Proc. Amer. Acad.*, xxiv., p. 327; also Chem. News, vol. lxxix., p. 163), and here also the simplest and most convincing way of settling the question was to determine directly the amount of cobalt present in the salt, thus obtaining its total percentage composition.

Of the three methods of procedure which presented themselves—precipitation, electrolysis, and reduction of the bromide—reduction by hydrogen was chosen as being the least complicated and most certain. The slight hope offered in the nickel research that electrolysis might be used for the determination of the metal was here lacking on account of the greater difficulty in obtaining a satisfactory electrolytic deposit.

A conceivable objection to the use of the reduction of an *oxide* as an accurate quantitative method is the possibility that this reaction may not be capable of absolutely complete fulfilment. It is well known, for example, that one is rarely able to re-oxidise wholly a metal once reduced, even if the material is finely divided. In the case of the oxide there is no means of deciding whether or not the last traces of oxygen have been removed, while in the case of the *bromide* a residue of halogen is easily detected. The complete reduction of nickelous bromide described in the preceding paper shows that some such operations are in fact possible. It is easy to see how the increase in volume involved in oxidation might cause a part of the metal to be permanently protected by the growing coat of oxide; on the other hand, an oxide or salt which is being reduced leaves only its skeleton behind, the innermost

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No 14, February, 1899.

meshes of which may be penetrated by the reducing agent.

Cobaltous bromide when heated in a current of dry hydrogen begins to be reduced at a temperature of about 350°. At higher temperatures the reduction goes on more rapidly, but is then accompanied by partial sublimation of the bromide. Schützenberger's (*Compt. Rend.*, cxiii., 177) observations on the sublimation of nickelous chloride were similar to these, but he seemed to think that some strange compound must have been the medium of the change, instead of realising that in the presence of hydro chloric acid a trace of the vapour of the metallic salt might easily exist even in an atmosphere of hydrogen.

If the hydrogen is *moist*, however, the action begins at a lower temperature, about 250°; but even under these conditions sublimation can be completely avoided only with the greatest difficulty. The reduction of *nickelous* bromide offered fewer difficulties: this process could be effected in a current of dry hydrogen, and without danger of sublimation of a trace of the material. The fact that moist hydrogen is more efficient than the dry gas is easily explained by the hypothesis that the oxide is formed as the first step in the reaction.

Purification of Materials.

Preparation of Cobaltous Bromide. — The cobaltous bromide used in this work was prepared by methods similar to those used in our previous investigation, and for details the previous paper should be consulted. Pure metallic cobalt was heated in a current of pure bromine and hydrobromic acid, and the sublimed bromide was preserved in weighing bottles contained in desiccators until used for analysis. Samples I. and II. were essentially the same as in the earlier investigation, even greater pains having been taken, however, in the purification of the reagents and water used in their preparation. Sample III. likewise was purified by essentially the same method as before, but was then further treated by six additional re-crystallisations as the purpureo-chloride, with the help of very pure re-distilled ammonia and hydrochloric acid. The oxides obtained from these preparations were finally reduced by means of pure hydrogen, instead of by ammonia as before.

Preparation of Bromine.—Here, also, the process of purification did not differ from that previously employed. The purity of the bromine is sufficiently proven by two analyses in which a known weight of silver was precipitated by a slight excess of ammonic bromide made from the halogen.

Ag in vacuum, Grms.	AgBr in vacuum. Grms.	AgBr : Ag.
2·91386	5·07226	57·447
2·97097	5·17170	57·447
	Average ..	57·447
	Stas found..	57·445

The balance and weights used in this work were the same as those described in our previous paper. The weights were carefully re-standardised, the values differing from those previously found by only a few hundredths of a milligrm. Since the balance was wholly free from iron, no inaccuracies could have arisen from magnetic attraction, either in this work or in that upon nickel.

Owing to the fact that the specific gravity of cobalt is almost identical with that of brass, no correction was required to reduce the weight of the cobalt to a vacuum standard.

The correction of +0·00010 grm. per grm. of cobaltous bromide was applied in each case to the weighings of that material. All weighings were made by substitution, as usual.

We are indebted to the Cyrus M. Warren Fund for Chemical Research, in Harvard University, for some of our more expensive pieces of apparatus.

Method of Analysis.

By means of the glass apparatus described in our earlier paper, cobaltous bromide, contained in a platinum boat, was dried in a current of pure dry nitrogen and hydrobromic acid gas in a hard glass tube heated to about 400°; and after the tube had been thoroughly swept out with nitrogen, and then by dry air, the boat was transferred to a weighing bottle in this safe atmosphere. The bottle was then weighed, and the boat carefully placed in the reduction tube, where it was heated in a current of moist hydrogen until the fumes of hydrobromic acid ceased to come off. The tube was then swept out with dry hydrogen, and when cool the boat was quickly replaced in the weighing bottle containing dry air, and was thus weighed after a suitable delay. In most analyses this process was repeated until the weight of the cobalt ceased to change. Cobalt reduced from the bromide is less constant in weight than nickel, gaining several tenths of a m.grm. in weight in twenty-four hours. For this reason the metal was always allowed to become thoroughly cool in the atmosphere of hydrogen, and the weighing bottle was allowed to come to perfect equilibrium with the atmospheric conditions inside a desiccator at the room temperature before receiving the boat. After half an hour *nickel* treated in the same way had been found to come to constant weight, and in half an hour the opportunity for oxidation of cobalt is so slight as to be negligible; hence this interval was the one which always elapsed between the bottling and the weighing of the cobalt. In one analysis, to see if exposure to the air affected the weight of the cobalt, the boat was bottled in dry nitrogen in the bottling apparatus, after being heated to constant weight in the usual way. Upon correcting the weight of the bottle for the difference in weight of nitrogen and air, the weights obtained by both methods agreed perfectly.

The resulting cobalt was in the form of a grey metallic sponge, which showed no traces of oxidation upon standing in air. Since previous work by other experimenters (Neumann and Streintz, *Monatshefte für Chem.*, xii., 642; *Berichte d. d. Ch. Gesell.*, xxv., 187 R; Hempel and Thiele, *Zeitschr. Anorg. Chem* , xi., 93) is not unanimous as to the occlusion of hydrogen by cobalt under these circumstances, it seemed desirable to us to obtain more evidence on this point. Accordingly, in several analyses the boat containing the cobalt was placed in a hard glass tube sealed at one end. After the air had been exhausted by means of a Sprengel pump, the tube was heated to about 500°, the highest temperature used in the reduction. In no case was a measurable quantity of gas evolved, and the cobalt did not lose in weight; hence it would appear that cobalt prepared from the bromide does not possess the property of occluding important amounts of hydrogen when heated in the gas.

To avoid any possibility of error, 2½ grms. of cobalt, freshly reduced from the bromide and allowed to cool in hydrogen, were subjected to quantitative combustion in the manner already described in the paper upon nickel. Only five-tenths of a m.grm. of water were formed; and even the repeated reduction and combustion of the residual oxide yielded only a m.grm. Evidently the amount of hydrogen occluded was very small. On the other hand, cobalt reduced originally from the oxide, when treated in the same way, was found to contain about fifteen times its volume of hydrogen, and when allowed to remain in hydrogen several hours it was found to have absorbed amounts comparable to those found by Neumann and Streintz (*loc. cit.*). A fuller statement of the experiments will be reserved for a future paper upon the nature and causes of these singular irregularities; for the present it is sufficient to have shown that cobalt, like nickel, reduced from the bromide, does not retain enough hydrogen to vitiate the results recorded below.

It is perhaps worth while to state also that the empty platinum boat was tested as to its power of absorbing weighable amounts of hydrogen. After ignition and

cooling in the gas, and bottling in dry air as usual, it was found to have gained 0·02 m.grm. when compared with its weight after ignition in air. Evidently the occlusion of hydrogen, if measurable at all, is balanced by absorption of air; hence for our purpose it may be neglected.

A slight sublimation of the cobaltous bromide took place during the reduction in almost every case. The amount of this sublimed material was determined by washing out the tube with a few c.c. of nitric acid, and evaporating this liquid to dryness. After the solution of the residue in water and the addition of an excess of ammonia, a very dilute standard solution of potassic permanganate was run in until a pink colour appeared. This method of Winkler's is applicable only when extremely small amounts of cobalt are present, because the brown colour of the cobaltic salt interferes seriously with the end point in the presence of large amounts of cobalt. The weight of the cobaltous bromide thus sublimed never amounted to more than three-tenths of a m.grm., and seldom exceeded one-tenth of a m.grm.

The platinum boat used in the earlier work served to contain the bromide in these experiments also. Although the metallic cobalt alloyed itself with the surface of the boat to a slight extent, we were able to remove completely the alloy by treating the inside of the boat with aqua regia. After this treatment and scrubbing with round sand, the boat showed no trace of darkening upon ignition. Evidently, then, the cobalt had been completely removed. Of course a gradual loss of weight took place, owing to solution of small amounts of platinum, but this loss amounted to only half a grm. in the course of the work.

(To be continued).

THE HODGKINS MEDAL.

A FEW weeks ago we announced the award of this Medal to Professor Dewar. With much pleasure we print the following letter from Professor Langley, accompanying the Medal.

Smithsonian Institution, Washington,
April 3rd, 1899.

DEAR SIR,

A Medal has been established under the name of the Hodgkins Medal of the Smithsonian Institution, which, in conformity with the will of its founder, is intended to be awarded only for exceptionally important contributions to our knowledge of the nature and properties of atmospheric air, or for practical applications of them to the welfare of mankind.

It gives me great pleasure to inform you, on the part of the Institution, that the first Gold Medal of the Hodgkins Foundation has been awarded to you in recognition of your indefatigable researches pursued for so many years, which have not only been potent in increasing and diffusing a more exact knowledge in regard to the nature and properties of air, but have opened the way for a practical utilisation of this knowledge in the advancement of human welfare.

I have now the honour to convey to you this Gold Medal accompanied by a duplicate impression in bronze, on behalf of the Smithsonian Institution, through the hands of the Ambassador of the United States in London, who, I am advised by the Department of State, is instructed to deliver it to you at the American Embassy in Victoria Street.

I beg to be allowed to add an expression of my gratification in being the medium by which this testimony of the Institution's admiration of your eminent services is conveyed, and of my personal regard.

I am, Sir, Yours with great respect,
(Signed) S. P. LANGLEY,
Secretary.

Professor James Dewar, F.R.S.,
Royal Institution,
London, England.

NOTICES OF BOOKS.

Report of the Council of the Institute of Mines and Forests, on the present Gold and Forest Industries of British Guiana, for the Year ending June 30, 1898. Georgetown, Demerara: Baldwin and Co. 1898. Pp. 23.

THE Council regret that they cannot report any marked progress in the industry; the amount of gold won has not fulfilled the hopes based on the large increase shown in the previous year, viz., 8911 ounces; it has, on the contrary, fallen below the production of 1895-96, and, in fact, is the lowest recorded for the last six years, viz., 117,265 ounces. This serious decrease is attributed to exceptionally bad weather, to the exhaustion of part of the alluvial workings, and to want of confidence arising from the unchecked dishonesty on the part of individuals entrusted with expeditions: this latter cause is, we are afraid, almost universal wherever there are gold-fields, and is to a large extent encouraged by the blind speculation on the part of the public, and the general ignorance of those responsible for the management and direction of the companies.

The amount of timber on which Royalty has been paid during this year is in excess of that for 1896-7, although the Customs returns are far less. This fact points either to the increase of local consumption or to large stocks being still on hand. The conservation of the valuable timber trees of the Colony is a matter the importance of which has been rather under-estimated in the past.

University College of Wales, Agricultural Department, Annual Report of Field Experiments. By J. A. MURRAY, B.Sc., and T. H. MIDDLETON, B.Sc. Aberystwith: J. and J. Gibson. 1898. Pp. 42.

Two sets of experiments have been carried out; the first on manuring grass land, with the object of finding out which of the commoner sources of phosphates and nitrogen are the most suitable for the district, and what are the most economical proportions in which to apply them.

The area under experiment is a little over an acre, divided into thirty-five plots. The field was dressed in parallel lines, I. to VII., with different quantities of phosphatic manures, and cross dressed in lines A to E, with different quantities of the nitrogenous manures. At the end of four years the conclusions drawn were:—1. Nitrogenous manures should not be used alone; 2. Phosphate manures may be safely used alone; 3. Basic slag is better than superphosphate; 4. Nitrate of soda is better than sulphate of ammonia; and 5. The most profitable dressing is 3 cwts. of basic slag and 2 cwts. of nitrate of soda per acre. The whole of the results of this experiment, however, show that any one manure will exhaust the land if applied continuously by itself for a sufficiently long time.

Another experiment was to find the most profitable dressing of basic slag, but no definite results have yet been obtained.

Further experiments were made on the effects of sodium chloride and sulphate on plants other than mangels, from which it was found that common salt is injurious to grass, and that the injurious effect is due to the chlorine and not to the sodium.

Another series of experiments on meadow-hay show that on the whole nitrate of soda has decreased the crop, superphosphate of lime has increased it, kainit has largely increased it, lime—in the absence of potash and in conjunction with nitrate of soda—has decreased the yield of hay, and that a mixture of 4 cwts. of kainit and 4 cwts. of superphosphate has given a profit of 200 per cent. These conclusions are all based on the average of twelve years.

We are pleased to see that the University of Wales is doing such useful work, and only hope that the farmers will take advantage of and profit by it.

Boron Food Preservatives, and their Influence on the Human Organism. London: Perkins, Bacon, and Co., Ltd. Pp. 63.

From the earliest times food has been preserved by means of salt, saltpetre, &c., but, as these bodies have only a slight antiseptic power, very large proportions had to be used; this has the effect of hardening and rendering meat less digestible, besides bringing on scurvy and scrofula. It has been found that boron possesses antiseptic properties far greater than that of salt or saltpetre, thereby rendering it possible to use a much smaller quantity. The new antiseptics have been largely used of late years, and among these one of the principal is boron.

The question has often been raised as to whether the continued use of boric acid was inimical to health; extracts from a large number of reports are here given to show that such is not the case. Fish, meat, butter, milk, bacon, &c., are all being preserved with borax, without impairing their nutritive qualities or having any deleterious effect on the health of the consumer. Of course a careful oversight must be exercised, and checks enforced as to the nature of the preservative used.

Borax appears to be the best of these antiseptics: it has no sour taste, and has no corrosive action on the skin; on the contrary, it is often used for allaying local inflammation. It possesses very slight physiological properties, is easily absorbed, and is quickly eliminated by the kidneys, whose secretions it promotes.

The results of a large number of experiments made by Dr. R. H. Chittenden, of Yale University, show that boracic acid and borax, when present in moderate quantities, have little or no deleterious effect upon the more important chemical processes of digestion; on the contrary, their presence may even accelerate the normal digestive processes of the alimentary tract.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 14, April 4, 1899.

Reduction of Phosphate of Calcium by Carbon in the Electric Arc.—Albert Renault.—Referring to the recently published paper of M. Moissan on crystallised phosphide of calcium prepared in the electric furnace, the author announces that during his recent work on the reduction by carbon in the electric arc of the phosphorus acids, he obtained the phosphide P_2Ca_3. The most important property of this substance is its power of decomposing water and evolving the hydrogen in the form of phosphoretted hydrogen; this latter being entirely absorbed by copper sulphate, and not being spontaneously inflammable in the air. Under certain conditions, the details of which will be published later, the author obtained a mixture of calcium phosphides which gave with water both gaseous and liquid phosphoretted hydrogen at the same time.

Acetone Oils from the Dry Distillation of Pyrolignite of Lime as a Source of Methylpropyl Ketones.—A. and P. Buisine.—Pyrolignite of lime contains always, besides acetate of lime, of which the major part consists, small quantities of calcium salts of the highest volatile fatty acids. The crude acetone leaves, on its rectification, about 5 per cent of oil passing over above 70°. This product the authors call oil of acetone; from it has been extracted acetone, methylethyl ketone, methylpropyl ketone, methylbutyl ketone, and methylisopropyl ketone. To separate the latter oils from the mixture, the whole is shaken up with an excess of concentrated solution of bisulphite of sodium. The mixture becomes a pasty mass, from which the solid and liquid parts separate after standing for some hours. The liquid is separated by filtration at the pump, and the solid part washed with bisulphite solution and then with ether, and dried in the air. The bisulphide compound is decomposed by an excess of hot sodium carbonate solution. An oil separates, which is decanted off and dried over dry potassium carbonate. When distilled, this oil passes over almost entirely between 90° and 110°, and consists of a mixture of methylisopropyl ketone and methylpropyl ketone. These two can be separated from one another by repeated rectifications, the methylpropyl ketone forming by far the larger portion of the mixture.

Solanine.—P. Cazeneuve and P. Breteau.—There is a great difference of opinion about the composition and properties of solanine. The authors have investigated the matter afresh; their product gives on analysis the simple formula $C_{28}H_{47}NO_{10}.2H_2O$. It differs from the solanines hitherto described in the phenomena of its coloration products when in contact with strong sulphuric, nitric, and hydrochloric acid.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., June 13, 1898.

Spectro-chemistry of Nitrogen.—J. W. Brühl.—The author has studied the optical properties of nitrogen and a series of its derivatives, principally:—(1) Nitrous and nitric acids, the nitrates, nitrites, and the nitro-carbides; (2) the hydrazines and the diazoïcs; (3) the oxynitro-derivatives; (4) the nitrosamines and the nitrosamides; (5) the nitramines and the nitramides; (6) protoxide of nitrogen, molecular nitrogen, and oxygen. His conclusions are that, in ammonia, hydroxylamine, the primary amines, and substituted hydrazines, nitrogen possesses the same atomic refraction. The atomic refraction of nitrogen is more feeble in the tertiary and secondary amides than in the corresponding amines. In binoxide of nitrogen, the refraction of the group NO is more feeble than in the nitrosamines and the alcoholic nitrites. The refraction of the group $\overset{R}{\diagdown}\!\!>\!\!N-N$ is stronger than that of the ethylenic group. The nitramides, nitro-urethanes, &c., approach the groups N_2O_2 and NO_2. The nitrocarbides are comparable with the alcoholic nitrites. Nitrous acid in solution should have the formula $N(OH)_3$ or HO.NO; and nitric acid, its ethers and its salts, the formula RO—O—N=O.

Spontaneous Racemisation.—P. Walden.—Already noticed.

On Monobromacrolein and Tribromopropionic Aldehyde.—O. Piloty and A. Stock.—Non-polymerised bromacrolein is prepared by passing a vigorous current of steam through a solution of 30 grms. of acetate of soda in 80 c.c. of H_2O to which 100 grms. of dibromopropionic aldehyde has been added. The bromised aldehyde passes off with the first 100 c.c. Separate by decantation, dry over $CaCl_2$, and distil *in vacuo*. Bromacrylic aldehyde is a mobile colourless liquid, with a very pungent odour. Its formula is $CH_2=CBr—CHO$; it boils at 28·5° under 11 m.m., and at 111° under 420 m.m.; at normal pressure it boils at 120°, with partial decomposition; it is soluble in alcohol, ether, and warm water. It fixes bromine in the cold, forming tribromopropionic aldehyde, $CH_2Br.CBr_2.CHO$, boiling at 155° at the normal pressure, with decomposition; it is soluble in the organic solvents and in cold water.

The Tautomeric Forms of the α-Ketonic Ethers.—R. Schiff.—The chloralide of acetylpyruvic acid is obtained by heating acetyl-pyruvic ether with an excess of 3 mols. of anhydrous chloral to 100° in a closed vessel for three hours. The product is purified by crystallisation in benzene; it forms hard prisms fusible at 138°, soluble in alcohol, ether, warm water, and boiling benzene. The

chloralide of benzoylpyruvic acid is prepared in a similar fashion, but by heating to 150°. The hard crystals, analogous to the others, are fusible at 198°.

Action of Benzylidene Aniline on the Ethers of the Non-saturated Oxy-acids.—R. Schiff and L. Gigly.—Acetonoxalic ether and benzylidene aniline unite molecule for molecule at the temperature of the water-bath, forming dihydrodiphenyldicetoacetylpyrrol; it crystallises in boiling amylic alcohol in needles which decompose at about 240°. Heated with hydroxylamine, it gives an oxime corresponding to the ketonic form, fusible at 215°. Pyruvic acid unites with benzylidene-aniline in acetic solution, forming dihydrodiphenyldicetopyrrol; it is a yellow powder, decomposing at 148°.

Action of Sodium on Dimethylacetylacetic Ether.—M. Conrad and R. Gast.—If we heat 86 grms. of dimethylacetylacetic ether to 110—120°, and gradually add 7 grms. of sodium, hydrogen is given off, and we obtain a white mass formed of a mixture of two soda derivatives. Supersaturate with dilute H_2SO_4, exhaust with ether, and distil. The portion coming over at 90—92° (24 grms.) is isobutyrate of methyl; the fraction passing at 228—232° (30 grms.) is γ-acetyldimethylacetylacetic ether (α-dimethyltriacetic ether). The soda derivative is a white crystalline mass, which does not react with the alcoholic iodides even when warm. The oxime crystallises in white needles fusible at 115°, and is soluble in alcohol; the dioxime has not been obtained. By heating with dilute hydrochloric acid or with baryta-water to 120° in a closed tube, we obtain acetylisobutyrylmethane, a yellowish liquid boiling at 171°.

Some Cases of Tautometry.—R. Schiff.—Ethylene-diacetylacetic ether is easily prepared by dissolving two molecules of acetylacetic ether and one molecule of acetic aldehyde in two volumes of alcohol and adding a little piperidine; leave in a cool place for twenty-four hours and precipitate with iced water. Isomerisation is produced when the ether is heated with alcohol. The enolic form is obtained in crystals when ethylene-diacetylacetic ether is dissolved in two molecules of ethylate of sodium, and neutralised exactly in the cold with dilute HCl. To separate the two modifications of ethylene-diacetylacetic ether we can make use of the combinations of this latter with the aromatic aldehydic bases.

On Diacetone-hydroxylamine, and on the Stereo-isomeric Aliphatic Ketoximes.—C. Harries and L. Jablonsky.—The authors have succeeded in isolating the two possible modifications of the oxime and the oxide of mesityl,—

$$(CH_3)_2.C{=}CH.C.CH_3 \quad \text{and} \quad (CH_3)_2.C{=}CH.C.CH_3$$
$$\qquad\qquad\quad \| \qquad\qquad\qquad\qquad\quad \|$$
$$\qquad\quad HO{-}N \qquad\qquad\qquad\quad N{-}OH$$

On some Double Combinations of the Aromatic Ketones and Orthophosphoric Acid.—A. Klages and P. Allendorff.—Acetophenone unites directly with concentrated phosphoric acid, giving rise to the combination $C_6H_5.CO.CH_3+H_3PO_4$. It suffices to mix equimolecular quantities of the two substances. The ketone dissolves first, then the mass suddenly solidifies, with a considerable disengagement of heat; the product is then purified by crystallisation in ether. Phosphoric acid forms analogous combinations with other aromatic methyl ketones, and even with thienones. All these bodies are decomposed by water and by alcohol; they are equally decomposed if we attempt to distil them. Combinations of phosphoric acid with acetyl pseudocumene, and acetothienone are also described.

Action of Diazomethane on some Nitramines and on the Aromatic Nitro-derivatives.—J. L. Heinke.—Diazomethane reacts on the trinitro-derivatives, either by direct fixation or by giving rise to methyl-derivatives. Thus, with trinitrobenzene the reaction may be represented by the equation $C_6H_3N_3O_6+4CH_2N_2=C_{10}H_{11}N_5O_6+3N_2$. It acts on nitro-urethane in ethereal solution, giving nitrogen and methylnitramide.

MISCELLANEOUS.

Royal Institution. — On Tuesday next, May 2nd, Professor Silvanus P. Thompson, F.R.S., will deliver the first of a Course of Two Lectures at the Royal Institution, on "Electric Eddy Currents"; these are the Tyndall Lectures. On Thursday, May 4th, Mr. Lewis F. Day will begin a Course of Three Lectures, on "Embroidery"; and on Saturday, May 6th, Mr. W. L. Brown, L.R.C.P., will deliver the first of Two Lectures on "To Iceland in Search of Health." These lectures will be illustrated by the lantern. The Annual Meeting of the Members will be held on May 1st. The Friday Evening Discourse on May 5th will be delivered by Dr. W. J. Russell, F.R.S.: his subject is "Pictures produced on Photographic Plates in the Dark."

A New Method for the Estimation of Bismuth.—L. Vanino and E. Treubert.—If we heat, while stirring, a mixture of alkaline formaldehyd and a solution of a bismuth salt, the bismuth is completely precipitated in the metallic state. A slightly acid solution of the bismuth salt is mixed with the formaldehyd, and a large excess of a 10 per cent solution of caustic soda. The mixture is heated on the water-bath and continuously stirred, until the metallic bismuth is entirely deposited and the supernatant liquid becomes perfectly clear. We then add an excess of formaldehyd and caustic soda, and heat over a Bunsen for several minutes. The precipitate is washed by decantation with boiling water, then kneaded with a stirring-rod to bring it into a compact mass. It is collected on a tared filter or in a Gooch crucible, washed with absolute alcohol, and dried at 105° C. This reaction can be utilised for the separation of bismuth from certain other metals, such as aluminium, zinc, &c.—*Berichte*, xxxi. (9), p. 1303.

The Detection of Chromium in the presence of a Large Proportion of Iron.—A. Seyda.—The author has applied to this research a reaction which he seems to believe is new, but it was described nearly fifty years ago by A. Reynoso (*Ann. de Chim. et de Phys.*, 1851, [3], xxxiii., p. 324). The solution containing the mixture of the ferric and chromic salts is treated by an excess of an alkaline hydrate, then by permanganate of potash until the colour is persistent when warmed. After heating to about 100° for a quarter of an hour, the solution is cooled, and the excess of permanganate destroyed by means of a few drops of alcohol, and filtered. The chromium, transformed into an alkaline chromate, passes into the filtrate, which it colours yellow. If we desire any further characteristic of this compound, it is sufficient to acidulate with acetic acid, which will cause the pale yellow tint to change to an orange-yellow (dichromate); we then add one or two drops of plumbic solution; a bright yellow cloudiness is produced, due to the precipitation of plumbic chromate.—*Chem. Zeitung*, 1898, No. 22, p. 1085.

Merck's Digest.—Nos. 2 and 3.—These two numbers of this publication deal respectively with digitoxin and tropacocaine. Digitoxin is the most active glucoside contained in *Digitalis purpurea*. Its composition is represented by the formula $C_{28}H_{46}O_{10}$; it occurs as a white crystalline powder, soluble in alcohol and chloroform, slightly soluble in ether, and insoluble in water; it is stated that it possesses a quick, positive, and energetic action, and that untoward effects are seldom observed, and then only to a slight degree. The action manifests itself in from twelve to twenty-four hours; cyanosis and cardiac disturbances very often disappear by this time,—the pulse becomes strong and regular. It has also been found of advantage in pneumonia and typhoid. Tropa-

cocaine or benzoyl pseudotropein was first obtained from Javanese coca leaves, and afterwards prepared synthetically from the tropine obtained by the decompositon of atropine and hyoscyamine. Its hydrochlorate has the formula $C_8H_{14}NO(C_7H_5O)$.HCl, and occurs in colourless needles soluble in water and fusing at 271°. It is only half as toxic as cocaine, local stimulation is more rapidly produced and by less concentrated solutions, and recovery from its effects is more rapid. The action of tropacocaine on the nerve-centres is first stimulating, then paralysing from the brain down in decreasing degrees; but it prevents complete paralysis of the spinal cord or respiratory centres. Another advantage is that it keeps well in solution.

Carbonic Acid.—We understand that the Birmingham Oxygen Company are putting down in their works a large plant, of the most approved type, for the manufacture of pure carbonic acid gas under Steinem's and Murray's patents. Hitherto all supplies of this gas have been brought to the Midlands from London and Manchester, so that the plant must prove a valuable acquisition to the district.

MEETINGS FOR THE WEEK.

MONDAY, May 1st.—Society of Arts, 8. (Cantor Lectures). "Leather Manufacture," Prof H. R. Procter, F.I.C.

—— Royal Institution, 5. General Monthly Meeting.

TUESDAY, 2nd.—Royal Institution, 3. (The Tyndall Lectures). "Electric Eddy-currents," by Prof. Silvanus P. Thompson, D.Sc., F.R.S.

WEDNESDAY, 3rd.—Society of Arts, 8. "Ætheric Telegraphy," by W. H. Preece, C.B., F.R.S.

—— Society of Public Analysts, 8. "On some Comparative Analyses of, and Digestive Experiments with White and Whole-meal Breads," by O. Rosenheim, Ph.D., and P. Schidrowitz, Ph.D. "The Assay of Belladonna, B.P.," by F. C. J. Bird. "On the Use of Boric Acid and Formaldehyde as Milk Preservatives," by S. Rideal, D.Sc., and G. R. Foulerton, F.R.C.S. "The Value of the Estimation of Pentosans in Food Materials," by Otto Hehner and W. P. Skertchly.

THURSDAY, 4th.—Royal Institution, 3. "Embroidery," by Lewis F. Day.

—— Chemical, 8. "On the Combustion of Carbon Disulphide,' by H. B. Dixon and F. J. Russell. "The Action of Nitric Oxide on Nitrogen Peroxide," by H. B. Dixon and J. D. Peterkin. "On the Mode of Burning of Carbon," by H. B. Dixon. "Crystalline Glycollic Aldehyde," by H. J. H. Fenton and H. Jackson. "On the Blue Salt of Fehling's Solution and other Cuprotartrates," by O. Masson and B. D. Steele. "The Preparation of Acid Phenolic Salts of Dibasic Acids," by S. B. Schryver, D.Sc., Ph.D. "The Maximum Pressure of Naphthalene Vapour," by R. W. Allen, M.A.

FRIDAY, 5th.—Royal Institution, 9. "Pictures Produced on Photographic Plates in the Dark, by W. J. Russell, Ph.D., F.R.S.

SATURDAY, 6th.—Royal Institution, 3. "To Iceland in Search of Health" (with Lantern Illustrations), by W. L. Brown, L.R.C.P., L.R.C.S.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2058.

THE ACETONE OILS AS DENATURALISING AGENTS.

By M. KLAR.

A GREAT number of experiments have been made for the purpose of replacing wood-spirit and the pyridic bases by another denaturalising product offering more difficulties to the rectification of the denaturalised alcohol.

Dr. Lang, a Swiss chemist, has pointed out the conditions which a good denaturalising agent ought to fulfil; they are the following:—

1st. It should render the alcohol unfit for consumption.

2nd. It should not render alcohol more inflammable to any sensible extent, nor cause it when burning to give off toxic, fuliginous, or nauseous products.

3rd. The denaturalising material should be cheap and effective in small quantities.

4th. It should be easy to detect, and therefore not to be confounded with products normally present in alcohol of fermentation.

5th. Its chemical and physical properties should make the rectification of the alcohol so difficult that this operation cannot be carried on commercially with any advantage.

Dr. Lang thinks that the acetone oils answer these requirements; these oils are obtained as a by-product in the manufacture of acetone. The Swiss monopoly has bought 40,000 kilogrms. for a trial, and Dr. Lang has taken out a patent for the use of these oils as a denaturalising agent and for their preparation.

According to this patent, the portions distilled between 81° and 230° from commercial acetone comprise the higher homologues of acetone and of ethylmethylacetone, and can be utilised as denaturalising agents; in quantities of 1 per cent it makes the rectification of alcohol impossible, and in a much more certain manner than with the heavy benzenes used in France. If we take into account the low price of acetone oils,—about 36 francs per 100 kilogrms.,—and the small quantity shown by Dr. Lang to be sufficient, this method of denaturalising seems to possess great advantages; but we must also consider whether sufficient quantities of this substance (at present unused) can be manufactured, and if, with an increase in the demand, the output will be sufficiently great to prevent any rise in price.

Let us examine the possible sources of supply of the acetone oils. Dr. Lang quotes the following:—

1st. The higher acetones obtained as a by-product in the manufacture of methylacetone, by acetate of lime, from the distillation of wood.

2nd. The oils remaining after the rectification of raw wood-spirit.

3rd. The rectification of raw alcohols.

For this latter source M. Lang proposes a method of extraction which has never yet been carried out on the commercial scale,—that is to say, the oxidation of the fusel oils by means of a chromic mixture, the transformation of the volatile acids formed into salts of lime, such as the acetate, propionate, butyrate, and valerate, the desiccation of these salts and their dry distillation, which finally gives a mixture of ketones with a high boiling-point.

If we estimate the total annual consumption of denaturalised alcohol in Germany to be 50,000,000 litres, requiring 1 per cent of acetone oil, the quantity of oil necessary for its denaturalisation will be at least 500,000 litres. Let us see if the sources of supply proposed by Dr. Lang are able to furnish this quantity.

According to the most trustworthy sources of information there is produced in Germany 8,000,000 kilogrms. of acetate of lime, at the outside, to which must be added 9 000,000 kilogrms. of the same salt imported, or a total of 17,000,000 kilogrms. used for the production of acetone, and giving about 2 per cent of acetone oil, or about 350,000 kilogrms.; the rectification of 1,000,000 kilogrms. of raw acetone would give another 100,000 kilogrms. of acetone oil; there would therefore at present be a deficit of hardly 50,000 kilogrms. But it is in no way certain that the price would remain the same, and a syndicate might be formed.

As far as the acetone oils from the rectification of wood-spirit is concerned, the quantity may be put down at 200,000 kilogrms., but a part only of these oils could be used for denaturalising purposes.

As for the treatment of fusel oil, we ought not to rely upon it much, as it is in great demand; we find that in one year its price has risen from 25 to 55 per cent, and even at this price it is difficult to obtain as much fusel oil as is wanted. So this substance can hardly be looked upon as a source of supply.

M. Buisine has pointed out, as an important source of supply, the waste waters from wool washing; as a matter of fact a fermentation is set up in these waters which produces volatile fatty acids—acetic acid and capronic acid. It therefore suffices to distil this liquid in a current of steam, to obtain from 1 cubic metre of the water about 10 kilogrms. of acetic acid and 5 kilogrms. of propionic acid. As the towns of Roubaix and Tourcoing themselves give a daily supply of over 500 cubic metres of these wash waters, at least 12,500 kilogrms. of acetate of lime at 80 per cent, capable, according to M. Buisine, of giving a daily supply of 10,000 litres of acetone oils, can be obtained; but according to the author the return of oils would not be more than 3500 litres.

From the above data we are forced to the conclusion that Germany does not produce enough acetone oils to enable it to be used as the sole denaturalising agent, and that Lang's process for this country is of no practical interest. It would be otherwise if these oils were used as an alternative; for example, to replace wood-spirit for denaturalising in certain special cases; for instance, in 1895-96, 1,738,000 litres of alcohol at 100° were denaturalised with 5 per cent of wood-spirit; by replacing this with 1 per cent of acetone oil, only 17,000 kilogrms. of acetone oil, easy to procure economically, would have been required.

It has, further, been proposed to use, instead of wood-spirit, certain products therein contained, as a denaturalising agent. For instance, in 1881, Krämer and Lowenherz recommended allylic alcohol, which gave the desired result in proportions of 0·1 to 0·5 per cent in volume,—that is to say, ten or twenty times less than the acetone oil proposed by Dr. Lang. It certainly appears, however, from the above, that acetone oil cannot be considered as a substitute for wood-spirit.—*Zeit. f. Angew. Chemie*, 1898, p. 116.

Liquid Hydrogen.—At the Annual Meeting of the Members of the Royal Institution, held on May 1st, Professor Dewar made a brief reference to the recent scientific work of the Royal Institution, and announced that having obtained liquid hydrogen in considerable quantity he had directly determined its temperature and other physical constants, finding its boiling-point to be much lower than was previously supposed,—namely, 20 degrees above the zero of absolute temperature, and attaining by exhaustion a temperature of only 15 degrees absolute. Pending the discovery in quantity of some yet lighter gas, there was no means in sight of bridging this gap and reaching the zero point. He also took occasion to warn the public against absurd exaggerations as to the properties of liquid air, which, originating in America, found their way into popular magazines in this country.

ON A NEW COLOURED REACTION OF THE BENZOYL RADICAL.

By G. DENIGÈS.

By using formolised sulphuric acid at 2 per cent (40 per cent commercial formol, 2 c.c.; concentrated sulphuric acid, 100 c.c.), a reagent I have already used for differentiating the polyphenols, I have found a very convenient test for the benzoyl radical $C_6H_5.CO$, which exists in a certain number of biological products and medicaments, such as hippuric and benzoic acids, cocaine, &c.

To obtain this reaction it suffices to introduce into a test-tube a small quantity of a benzolised substance, 2 or 3 c.c. of the formolised reagent, and a thermometer; heat gradually and carefully; if the substance under examination contains the benzoyl radical, we obtain, at about 120°, a brownish red colouration, showing a wide but rather diffused absorption band in the green part of the spectrum. The reaction is very marked, and can be produced with a very small quantity of the benzolised compound. I have obtained this colouration very easily with—

Benzoic acid	$C_6H_5.CO.OH$
Chloride of benzoyl ..	$C_6H_5.CO.Cl$
Benzoyl acetic anhydride	$C_6H_5.CO.C_2H_3O_2$
Benzol acetic acid	$C_6H_5.CO.C_3H_5O_3$
Benzamide	$C_6H_5.CO.NH_2$
Hippnric acid	$C_6H_5.CO.NH.C_2H_3O_2$
Cocaine or methyl benzoyl ecgonine..	$C_6H_5.CO.C_{10}H_{16}NO_3$.

The derivatives in which the benzoyl is connected directly with the nitrogen, notably benzamide, require a rather longer contact at 120° than the other benzolised products, to give the desired colour.

The reagent used is coloured by other substances than the benzoyl derivatives, but the colouration in such cases generally shows itself at very different temperatures to 120°: this is the case with ordinary phenol; the polyphenols, the alkaloids of opium, &c., acting in the cold; and the salicylic products (salicylic acid, salicylamide). which decompose easily in warm phenol, in the presence of sulphuric acid, and colour this acid to which formol has been added, below 100°. Finally, the presence of the benzoyl radical may be hidden, if the nucleus to which it is fixed, or if the groups which surround it, are susceptible of reacting below 120° on the formolised sulphuric acid; such is the case with the ortho-forms and benzoic aldehyde.

With these reservations the coloured reaction just described may, if we observe the necessary precautions, be of great service for the identification of a considerable number of compounds used in pharmacy, or for the demonstration of the presence of the radical $C_6H_5.CO$, in certain natural or synthetic chemical bodies.—*Bull. de la Soc. de Pharm. de Bordeaux*, March, 1899.

SIXTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1898.*

By F. W. CLARKE.

(Concluded from p. 198).

The Didymiums.

JONES (*Am. Chem. Journ.*, xx., 345, May, 1898; CHEM. NEWS, lxxvii., 280) has determined the atomic weights of neodymium and praseodymium by means of the synthesis of the sulphates from the oxides. The material for the investigation was furnished by Waldron Shapleigh, and was very nearly pure. It was further purified by repeated fractional crystallisations of the double ammonium nitrates. From these salts the oxalates were prepared, and, from the latter, the oxides. The superoxide of praseodymium, Pr_4O_7, was reduced to Pr_2O_3 by ignition in hydrogen.

For praseodymium the results obtained were as follows, when O=16 and S=32·07:—

Weight Pr_2O_3.	Weight $Pr_2(SO_4)_3$.	Atomic weight Pr.
0·5250	0·9085	140·42
0·6436	1·1135	140·50
0·7967	1·3788	140·38
0·7522	1·3018	140·38
0·7788	1·3473	140·53
0·6458	1·1172	140·54
0·6972	1·2062	140·51
0·7204	1·2464	140·49
0·8665	1·4990	140·54
0·6717	1·1624	140·40
0·7439	1·2873	140·42
0·6487	1·1224	140·47
8·4905	14·6908	140·46

With O=15·88, Pr=139·41.

For neodymium the data are as follows:—

Weight Nd_2O_3.	Weight $Nd_2(SO_4)_3$.	Atomic weight Nd.
0·8910	1·5296	143·58
0·7880	1·3530	143·51
0·9034	1·5509	143·57
0·7668	1·3166	143·51
0·8908	1·5296	143·49
0·8848	1·5194	143·46
0·8681	1·4903	143·57
0·8216	1·4103	143·62
0·8531	1·4646	143·56
0·8711	1·4957	143·50
0·8932	1·5332	143·62
0·8893	1·5268	143·55
10·3212	17·7200	143·55

This value for neodymium must be corrected for the presence of a little praseodymium, which was estimated by the intensity of its lines in the spectrum. Corrected it becomes 143·6, or 142·52 when O=15·88.

It is noteworthy that the values found by Jones almost absolutely reverse those given by von Welsbach, who puts praseodymium at 143·6 and neodymium at 140·8. Possibly the error in the latter figures may be only typographical.

Another determination of the atomic weight of praseodymium is due to C. von Schele (*Zeit. Anorg. Chem.*, xvii., 319), who worked up 100 kilos. of monazite to obtain his material for investigation. Two methods of determination were tried: one by synthesis of sulphate from oxide, the other based upon the oxalate. The oxide itself was prepared from the oxalate, and reduced from Pr_4O_7—or, as von Schele gives it, PrO_2—to Pr_2O_3, by ignition in hydrogen. Disregarding a preliminary series of experiments made with impure material, and also the oxalate series, which gave unsatisfactory results, the final data are as follows:—

Weight Pr_2O_3.	Weight $Pr_2(SO_4)_3$.	Atomic weight Pr.
0·6872	1·1890	140·30
0·7834	1·3550	140·46
0·6510	1·1260	140·45
0·7640	1 3216	140·42
0·5183	0·8967	140·32
	Mean	140·40

This value, computed with O=16 and S=32, is sensibly identical with that found by Jones.

In the case of neodymium a single determination of

* *Journal of the American Chemical Society*, xxi., No 2,

atomic weight has been published by Boudouard (*Comptes Rendus*, cxxvi., 900). 2·758 grms. of sulphate gave 1·605 of oxide, or 58·194 per cent. Hence, with O=16 and S=32, Nd=143·045.

In this connection the spectroscopic work of Demarçay (*Comptes Rendus*, cxxvi., 1039), may also be properly noted. This chemist has studied the spectrum of neodymium obtained from diverse sources, and finds it to be definite and uniform. He therefore concludes that the metal is a distinct element, and not, as some chemists have thought, a mixture.

A preliminary notice, by Brauner (CHEM. NEWS, lxxvii., 161, April 7, 1898), of determinations of atomic weight upon the two metals in question, has also appeared. The material studied was obtained from Dr. Shapleigh, the determinations being made by the sulphate and oxalate methods. For praseodymium he obtained values ranging from 140·84 to 141·19, the average of thirteen determinations being Pr=140·95.

Neodymium gave values from 143·4 to 143·63, but the material used still contained $2\frac{5}{6}$ per cent of praseodymium. Here, again, Welsbach's figures are reversed.

Miscellaneous Notes.

In a series of papers, Daniel Berthelot (*Compt. Rend.*, cxxvi., 954, 1030, 1415, and 1501) shows that the true molecular weights of gases can be computed from their normal densities with the help of their coefficients of compressibility. By suitable mathematical formulæ, from existing data, he computes the following values, taking O=16 as his standard of comparison.

H	= 1·0074	
N	= 14·005	From N and N_2O.
C	= 12·005	From CO, CO_2, and C_2H_2.
A	= 39·882	
Cl	= 35·479	From HCl.
S	= 32·046	From SO_2.

From the density of nitrogen he finds N=14·000; and from nitrous oxide, N=14·007. These values he regards as superior to those determined by Stas, which are much higher; but Vézes (*Comptes Rendus*, cxxvi., 1714), in a critical note, expresses the contrary opinion. After all, a mathematical discussion of data depends for its ultimate value upon the accuracy of the data, and an exact theory applied to inexact material may yield inferior results. It may well be asked, therefore, whether the experimental data discussed by Berthelot are superior to those furnished by the researches of Stas—and this is the real point at issue. So far, the work of Stas does not seem to be overthrown.

The paper by Dulk (*Ber. d. Chem. Ges.*, xxxi., 1865, July 25, 1898), "Atomgewicht oder Atomgravitation," is essentially an abstract or summary of a book. Starting with H=1, by a system of geometric configurations, the author computes a series of values for atomic weights, which are sometimes curiously near the experimental determinations. The following atomic weights are computed:—

Li	7·0	B	11·041
Na	23·06	C	11·9497
K	39·111	Si	28·0
Rb	84·96	Cu	63·339
Cs	131·1	Ag	107·717
Cl	35·464	Au	195·77
Br	79·666	Hg	198·45
I	126·23	Zn	65·385
N	14·0	Cd	112·0
O	16·0	Tl	204·298
F	18·928		

New Tables.

Two new tables of atomic weights have appeared during the year; one by Richards (*Am. Chem. Journ.*, xx., 543, July, 1898), the other by a Committee of the

	Clarke.			
	H = 1.	O = 16.	Richards.	German.
Aluminum	26·91	27·11	27·1	27·1
Antimony	119·52	120·43	120·0	120·
Argon	?	?	39·9	40·
Arsenic	74·44	75·01	75·0	75·
Barium	136·39	137·43	137·43	137·4
Bismuth	206·54	208·11	208·0	208·5
Boron	10·86	10·95	10 95	11·
Bromine	79·34	79·95	79·955	79·96
Cadmium	111·54	112·38	112·3	112·
Cæsium	131·89	132 89	132·9	133·
Calcium	39·76	40·07	40·0	40·
Carbon	11·91	12·00	12·001	12·00
Cerium	138·30	139·35	140·0	140·
Chlorine	35·18	35·45	35·455	35·45
Chromium	51·74	52·14	52·14	52·1
Cobalt	58·55	58·99	59·00	59·
Columbium	93·02	93·73	94·0	94·
Copper	63·12	63·60	63·60	63·6
Erbium	165·06	166·32	166·0	166·
Fluorine	18·91	19·06	19·05	19·
Gadolinium	155·57	156·76	156 0	—
Gallium	69·38	69·91	70·0	70·
Germanium	71·93	72·48	72·5	72·
Glucinum	9·01	9·08	9·1	9·1
Gold	195·74	197·23	197·3	197·2
Helium	?	?	4·0	4·
Hydrogen	1·000	1·008	1·0075	1·01
Indium	112·99	113·85	114·0	114·
Iodine	125·89	126·85	126·85	126·85
Iridium	191·66	193·12	193·0	193·
Iron	55·60	56·02	56·0	56·
Lanthanum	137·59	138·64	138·5	138·
Lead	205·36	206·92	206·92	206·9
Lithium	6·97	7·03	7·03	7·03
Magnesium	24·10	24·28	24·36	24·36
Manganese	54·57	54·99	55·02	55·
Mercury	198·49	200·00	200·0	200·3
Molybdenum	95·26	95·99	96·0	96·
Neodymium	142·52	143·60	143·6	144·
Nickel	58·24	58 69	58·70	58 7
Nitrogen	13·93	14·04	14·045	14·04
Osmium	189·55	190·99	190·8	191·
Oxygen	15·88	16·00	16·000	16·00
Palladium	105·56	106 36	106·5	106·
Phosphorus	30 79	31·02	31·0	31·
Platinum	193·41	194·89	195·2	194·8
Potassium	38·82	39·11	39·140	39·15
Praseodymium	139·41	140·46	140·5	140·
Rhodium	102·23	103 01	103·0	103·0
Rubidium	84·78	85·43	85·44	85·4
Ruthenium	100·91	101·68	101·7	101·7
Samarium	149·13	150·26	150·0	150·
Scandium	43·78	44·12	44·0	44·1
Selenium	78·58	79·17	79·0	79·1
Silicon	28·18	28·40	28·4	28·4
Silver	107·11	107·92	107·93	107·93
Sodium	22·88	23·05	23·050	23·05
Strontium	86·95	87·61	87·68	87·6
Sulphur	31·83	32·07	32·065	32·06
Tantalum	181·45	182·84	183·0	183·
Tellurium	126·52	127·49	127·5	127·
Terbium	158·80	160·00	160·0	—
Thallium	202·61	204·15	204·15	204·1
Thorium	230·87	232·63	233·0	232·
Thulium	169·40	170·70	170·0	—
Tin	118·15	119·05	119·0	118·5
Titanium	47·79	48·15	48·16	48·1
Tungsten	183·43	184·83	184·4	184·
Uranium	237·77	239·59	240·0	239·5
Vanadium	50·99	51·38	51·4	51·2
Ytterbium	171·88	173·19	173·0	173·
Yttrium	88·35	89·02	89·0	89·
Zinc	64·91	65·41	65·40	65·4
Zirconium	89·72	90·40	90·5	90·6

German Chemical Society, consisting of Professors Landolt, Ostwald, and Seubert (*Berichte der Chem. Ges.*, xxxi., 2761, November 28, 1898). Both tables coincide in the main with that of your Committee, but in some instances there are differences which can be eliminated only by new investigations.

Richards's table is preceded by a careful discussion of some points at issue, especially as regards the atomic weights of antimony, cadmium, calcium, magnesium, platinum, tungsten, and uranium. For antimony, Richards prefers the value 119·92—or, in round numbers, 120—which depends on Cooke's analyses of the bromide, and involves the rejection of other data which seem entitled to some weight. For cadmium he accepts the higher value 112·3, rather than 112. Morse and Arbuckle's recent work lead me to adopt the value 112·38 for the present, bringing the Committee table into harmony with that of Richards. In the case of calcium, Richards regards the value 40·07 as too high, and adopts the round number 40. For magnesium, two values are in controversy, and here again Richards accepts the higher; in this case more evidence is needed. The same thing is true of platinum, tungsten, and uranium. The atomic weights of all three are uncertain to some tenths of a unit at least, and where Richards has selected data, I have preferred to use least square averages. New and better determinations are necessary in all three cases.

The Committee of the German Chemical Society present their table without discussion of the data, so that it represents their careful judgment as to the best values for analytical use, unencumbered by argument. All three of the members, however, argue at length in favour of O=16, as the basis of the scale, and give the well-known reasons in support of that view. Apart from theory, the oxygen scale certainly has the merit of greater convenience. The Committee also suggest the desirability of an international commission upon atomic weights, and in that all chemists are likely to agree.

In the accompanying table of atomic weight your Committee give first its own sets of values, based upon both standards, H=1 and O=16. These values are only rounded off to the second decimal place, and represent, so far, the actual results of re-calculation from the original data. Next is given Richards's table, and finally the table of the German Chemical Society, both sets of constants being more or less rounded off by the authors for convenience in practical use. It will be seen at once that the values adopted are in most cases sensibly identical. The new elements coronium, polonium, radium, monium, etherion, krypton, neon, xenon, and metargon are omitted, for lack of sufficiently precise data.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

Second Paper.—The Determination of the Cobalt in Cobaltous Bromide.

By THEODORE WILLIAM RICHARDS
and
GREGORY PAUL BAXTER.

(Continued from p. 201).

In the first two determinations the hydrogen was generated from hydrochloric acid by means of pure zinc. It was purified by passing through bulbs containing silver nitrate, potash, silver nitrate again, then through a hard glass tube heated to redness. From this point the gas came in contact only with glass, being conducted through three towers containing glass beads moistened with silver nitrate, then by means of T-tubes, either directly in a moist state or through a long drying tube containing stick potash, into the reduction tube. The reduction tube was connected with the rest of the apparatus by means of a ground-glass joint.

A small amount of white sublimate, which appeared beyond the boat during each of the preliminary ignitions, proved to be ammonic bromide. The source of the ammonia was not at first apparent, as it was hard to believe that the cobaltous bromide could retain ammonic bromide at a temperature between 400° and 500°. Upon examination of the silver nitrate columns it was found that reduction had taken place there, metallic silver being precipitated upon the beads.

(The fact that silver nitrate is reduced by molecular hydrogen has already been noted by other experimenters: Russell, *Journ. Chem. Soc.*, 1874, [2], xii., 3; Pellet, *Compt. Rend.*, lxxviii., 1132).

Of course the reduction of the silver alone could do no harm; but unfortunately it was attended by a reduction of the nitric acid also. This was proved by passing the resulting gas through a hot tube, when traces of ammonia were formed, capable of easy detection by Nessler's reagent. We had come face to face with one of those frequent cases where an attempt at purification had introduced a flaw as serious as the one it eliminated. The very common use of argentic nitrate as a means of purifying hydrogen is obviously a pernicious one, if accurate results are desired.

The hydrogen apparatus was then entirely re-modelled. Owing to the fact that the amount of hydrogen required for the completion of a reduction was very much larger than the amount actually necessary to combine with the bromine (see the preceding paper, *Proc. Amer. Acad.*, xxiv., p. 333), a gasometer was constructed which should collect the hydrogen after it had passed through the tube and deliver it repeatedly to the apparatus, after removal of the hydrobromic acid. The hydrogen was generated by a primary battery consisting of zinc amalgam, hydrochloric acid, and platinised platinum. The gas delivered by this apparatus is pure, except for the presence of a little hydrochloric acid, which can be removed easily by means of potash. The accompanying cut shows the apparatus in its improved form.

The bottle B is filled with pure hydrogen generated by the battery C. From the bottle A water is syphoned into B, forcing the hydrogen by way of the stopcock *e* through the column D, filled with beads moistened with aqueous cupric sulphate to remove sulphur compounds taken from the rubber; through the columns E and F, which contain dilute sodic hydrate, then either directly through *g* or through a potash tube G into the reduction tube H. After being freed from hydrobromic acid in the bottle K containing potash, the gas is conducted through the open stopcock *b* into A. When B is full of water the process can be repeated by interchanging A and B, and opening the stopcocks *c* and *d* after closing *b* and *e*. The generator C served to keep the pressure always outward. The current of gas could be regulated by a pinchcock *a* on the rubber syphon tube. This apparatus proved entirely satisfactory, and was not altered during the investigation.

As in the case of nickel, it was found impossible by reduction alone to remove the last traces of bromine from the spongy cobalt. Even long-continued heating to a temperature much above the subliming-point of cobaltous bromide failed to give complete reduction, the solutions of the reduced cobalt giving decided tests for bromine. In the first analysis this bromine was precipitated with an excess of silver nitrate and weighed. In Analyses 2, 3, and 4 the cobalt was leached with pure water, and after filtration the bromine was determined in the filtrate. The solutions of the cobalt in dilute nitric acid proved almost entirely free from bromine, that obtained from Analysis 4 being entirely so. The silver bromide from these solutions was combined with that obtained from the aqueous extracts and weighed. As it was hard to believe that cobaltous bromide could be enclosed by the reduced

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, Vol. xxxiv., No 14, February, 1899.

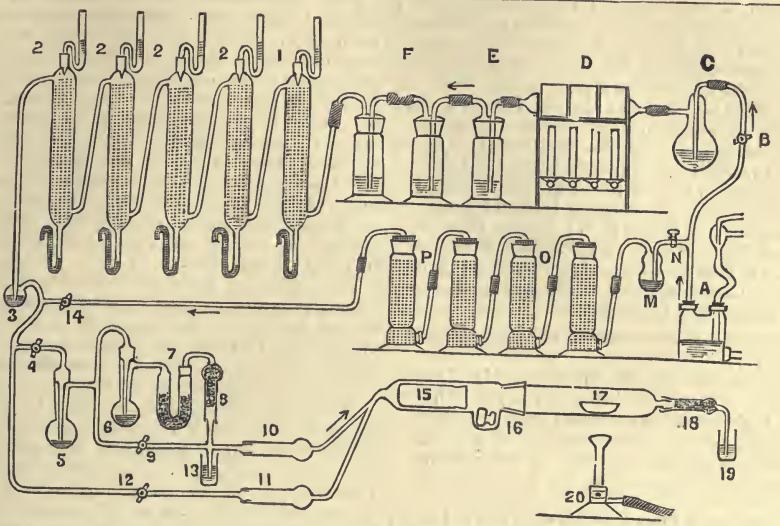


Fig. 1.—Apparatus for Igniting Cobaltous Bromide in any Desired Mixture of Gases.
The use of rubber was confined to the first part of this train, where it could do no harm (A B C D E F and A M N O P).

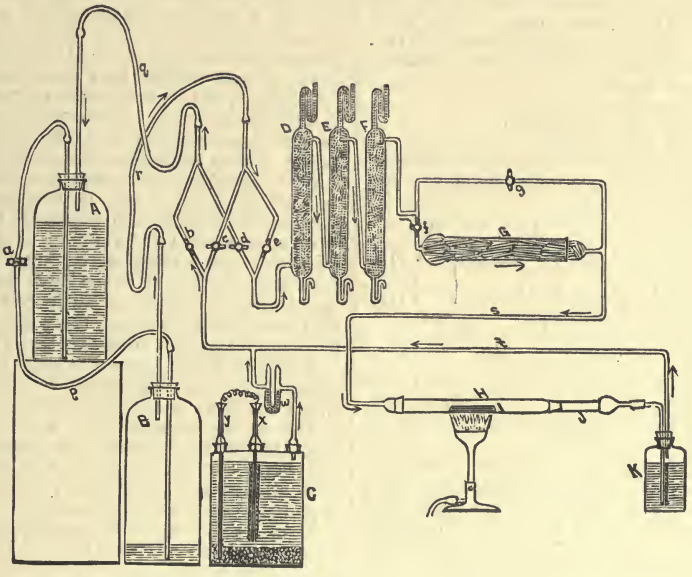


Fig. 2.—Apparatus for Reducing the Bromide.

cobalt in such a way as to remain unreduced and yet to go completely into solution with apparent ease, it was obvious that some foreign bromide must be present. Accordingly the filtrate from one of the precipitates of silver bromide was treated with an excess of hydrobromic acid, in order to remove the silver, and the re-filtered solution was evaporated to dryness. Upon a careful qualitative analysis tests were obtained for nothing but sodium and traces of cobalt. The sodium evidently came from the porcelain tube used in the sublimation, and we were dealing with an impurity precisely similar in source and nature to that described in the case of nickelous bromide. As the two investigations progressed side by side, the discovery was almost simultaneous in the two cases. We have already said that this outcome was not an unexpected one.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 20th, 1899.

Professor Thorpe, F.R.S., President, in the Chair.

Messrs. A. J. While, W. J. Sell, and S. Godfrey Hall were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Henry Aders, 28, St. John's Wood Road. N.W.; Percy Bean, 42, Granville Road, Blackburn; Walter Lionel Blackman, Mostyn, Mount Nod Road, Streatham, S.W.; Wilfred Carpmael, 24, Southampton Buildings, Chancery Lane, W.C.; Frederick Doyle, 8,

Woodlands Terrace, Middlesbrough; Frederick Charles Dunscombe, 54, Woodstock Road, Bristol; William Frederick Eichenauer, 58A, Maryon Road, Old Charlton, Kent; Friedrich Noel Ashcroft Fleischmann, Magdalen College, Oxford; Frederick Hutton Getman, 196, Atlantic Street, Stamford, Conn., U.S.A.; Julius Hübner, 24, Delanney's Road, Crumpsall, Manchester; Edward Charles Johnson, Lithgow, N.S.W., Australia; Arthur Alexander Leon, 13, Cleveland Square, Hyde Park, W.; James McAlley, Bankside, Falkirk; George Alfred Parkes, Muckomore Bleach Works, Co. Antrim, Ireland; Stanley John Peachey, 48, Grange Road, S.E.; Sidney Rossiter, 19, Ranelagh Road, West Green, N.; William Frederick John Shepheard, 12, Bridge Street Row, Chester; John Ward Stainer, 103, Cheriton Road, Folkestone; George Hardstaff West, Frankwell, Llanidloes.

The following Certificate was authorised by the Council under Bye-law I. (3):—

Bennetts, Benjamin Harvey, Gormanston, Mt. Lyell, Tasmania. Assayer. Two years' Student at the School of Mines, Ballarat, Victoria. At present Assayer for the Mount Lyell Mining and Railway Company, Tasmania.

Albert H. Turton. Harold Harris. *John Provis.*

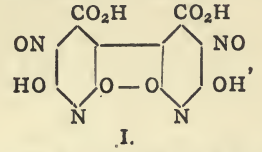
Of the following papers those marked * were read:—

* 48. "*The Synthesis of some ββ-Dipyridil Derivatives from Citrazinic Acid.*" By W. J. SELL, M.A., and H. JACKSON, B.A., B.Sc.

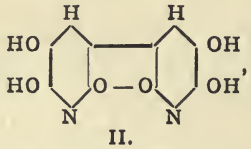
The present communication deals mainly with the constitution of some of the compounds described by Sell and Easterfield (*Trans.*, 1893, lxiii., 1035), of which little more than an analysis and brief description were given. It is now shown that citrazinic acid yields a nitroso-derivative, to which the formula—

$$CO_2HC\begin{matrix}=CH_2-\!\!-CO\\ =CNO-C(OH)=N\end{matrix}$$

may be assigned. This compound is readily oxidised by nitrous or nitric acids, producing the yellow acid represented by formula I.—



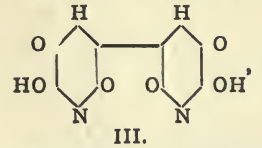
I.



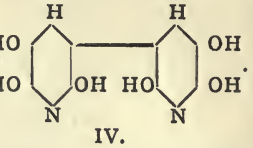
II.

Both these substances, on reduction, readily yield a very sparingly soluble compound having a bronze-like appearance, and possessing the constitution represented by formula II.

The bronze-like substance reacts readily when boiled with fuming hydriodic acid and phosphorus, producing *αα'*-diglutaric acid, thus showing that these substances are derivatives of dipyridyl. With nitric acid it produces a golden-yellow, crystalline compound, to which the authors assign the constitution represented by formula III,—



III.



IV.

This substance is readily reduced to the bronze-like compound, and further reduction, either by hydriodic acid or stannous chloride, produces the hexhydroxy derivative having the constitution represented by formula IV.

If the bronze-like substance be heated at 100° with chlorosulphonic acid, a white, crystalline compound, having the formula $C_{10}H_4Cl_2O_3$, is produced.

*49. "*Action of Hydrogen Peroxide on Carbohydrates in the presence of Iron.*" By R. S. MORRELL, M.A., Ph.D., and J. M. CROFTS, B.A., B.Sc.

Cross and Bevan, in their paper on the reaction of carbohydrates with hydrogen peroxide (*Trans.*, 1898, lxxiii., 463), showed that substances which reacted with phenylhydrazine in the cold were formed. In September, 1898, some results of the reaction were communicated to the British Association, in which it was shown that the first product was undoubtedly glucoson. The glucoson had not then been isolated, but was identified by means of the osazone formed by the action of phenylhydrazine *in the cold*, and by the isolation of the methyl phenyl glucosazone, precipitated also in the cold. The formation of this methyl phenyl glucosazone was considered by Fischer to be one of the characteristic tests for the presence of glucoson.

The action of hydrogen peroxide in the presence of ferrous salts has been extended to levulose and galactose, to the pentose arabinose, and to the methyl pentose, rhamnose. Of these, levulose and arabinose have yielded results which are similar to those obtained with glucose, namely, the formation of an oson.

The oson was detected, in the case of glucose, by the formation, in each instance in the cold, of phenyl glucosazone (m. p. 205°), and of methyl phenyl glucosazone (m. p. 152°), both the glucosazones being analysed. The solution of the glucoson reduces Fehling's solution in the cold, and more strongly so on slightly warming. It yields precipitates in the cold with diamines, with hydrazine, and with substituted hydrazines.

It might be that the osazones were formed from the glucose directly, and not from the oson; the solution, however, after fermentation at 30°, was still found to react quite as readily with hydrazines in the cold. A small quantity of the oson isolated was found to have properties like those ascribed by Fischer to glucoson.

The behaviour of levulose is almost identical with that of glucose under like conditions of treatment. The oson formed is glucoson, and its identification rests on the same evidence as that given for glucoson from glucose.

With regard to arabinose, the action is again similar to that which takes place in the case of the hexoses. Arabinoson is undoubtedly formed, and its identification is established by the formation of arabinosazone in the cold, and more completely by the formation of methyl phenyl arabinosazone in the cold, whereas arabinose and methyl phenyl hydrazine, even with excess of the hydrazine and after warming on the water-bath, were found to form methyl phenyl arabinose hydrazone.

Galactose and rhamnose, under like conditions of treatment, also form substances of the nature of an oson, which are being investigated.

The action of bromine at 40° on the solution of the glucoson gives a liquid still strongly reducing, which reacts easily with phenyl-hydrazine, and forms, in the case of levulose, a soluble calcium salt of a dibasic acid, which is probably an oxysaccharic acid.

The course of the reactions may, perhaps, be expressed by the following equations:

$$\underset{\text{Glucose.}}{CHO\cdot CHOH\cdot(CHOH)_3\cdot CH_2OH} + O = \underset{\text{Glucoson.}}{CHO\cdot CO\cdot(CHOH)_3\cdot CH_2OH} + H_2O.$$

$$\underset{\text{Levulose.}}{CH_2OH\cdot CO\cdot(CHOH)_3\cdot CH_2OH} + O = \underset{\text{Glucoson.}}{CHO\cdot CO\cdot(CHOH)_3\cdot CH_2OH} + H_2O.$$

$$\underset{\text{Arabinose.}}{CHO\cdot CHOH\cdot(CHOH)_2\cdot CH_2OH} + O = \underset{\text{Arabinoson.}}{CHO\cdot CO\cdot(CHOH)_2\cdot CH_2OH} + H_2O.$$

DISCUSSION.

Mr. FENTON said that he was very glad that Dr. Morrell had succeeded in bringing his observations on carbohydrates to the present stage. His results now nearly completed the series of investigations which had been

undertaken with a view of studying the behaviour of typical hydroxy-compounds towards oxidising agents in presence of iron.

*50. "*The Condensation of Oxalic Acid and Resorcinol.*" By John Theodore Hewitt and Arthur Ernest Pitt.

The condensation of oxalic acid and resorcinol, on heating with concentrated sulphuric acid, has been studied by von Baeyer (*Ber.*, 1871, iv., 662) and Gukassianz (*Ber.*, 1878, xi., 1184). The former stated that the product obtained closely resembled euxanthone, the latter that two isomeric substances were formed, both having the formula $C_{14}H_8O_5$, but whilst one was soluble in alcohol and gave non-fluorescent alkaline solutions, the other was insoluble in alcohol, but dissolved in alkalis with a fine moss-green fluorescence.

The authors have studied the former of these two products, which is the chief product of the reaction. It is distinct from the substances obtained by Claus and Andreæ (*Ber.*, 1877, x., 1305; 1881, xiv., 2563) and von Georgievics (*Mitt. Technol. Gewerb-Mus. Wien*, 1898 [ii.], viii., 364). These chemists used an excess of oxalic acid as a condensing agent, and employed a higher temperature. Gukassianz misinterpeted the results obtained on combustion; his compound really has the formula $C_{20}H_{14}O_7$, and is probably a carboxylic acid. In addition to further analyses of this compound, the authors describe the following derivatives:—

Sodium and lead salts, $C_{20}H_{13}O_7Na$,$(C_{20}H_{13}O_7)_2Pb$. Triacetylated lactone, $C_{20}H_9O_6(C_2H_3O)_3$. Triacetylated acid, $C_{20}H_{11}O_7(C_2H_3O)_3$. Tetracetylated lactone of leuko-acid, $C_{20}H_{10}O_6(C_2H_3O)_4$. Product obtained from acid and benzoyl chloride, (?) $C_{14}H_7O_5(C_6H_5CO)$. Dinitro-lactone, $C_{20}H_{10}(NO_2)_2O_6$. Sodium salt of dinitro-acid, $C_{20}H_{11}(NO_2)_2O_7Na$. Triacetylated dinitro-lactone, $C_{20}H_7(NO_2)_2O_6(C_2H_3O)_3$. Tetrabrominated acid, $C_{20}H_{10}Br_4O_7$.

From the composition of the compounds described, the authors consider that the acid must be represented by the formula $[C_{18}H_9(:O)(OH)_4]:C\cdot CO_2H$.

51. "*Ethyl Ammonium Sulphite.*" By Edward Divers and Masataka Ogawa.

Dissolved in alcohol, sulphur dioxide and ammonia combine with each other and the alcohol to form a new salt, ethyl ammonium sulphite, which is a crystalline solid, subliming undecomposed in dry air, soluble in alcohol, insoluble in ether, and at once changed by water into alcohol and ammonium pyrosulphite. Hence, in preparing the salt, the absence of water must be carefully secured. Ethyl ammonium sulphite belongs to the series of new sulphites, or metal-sulphonates discovered within the last few years:—Phenyl sodium sulphite (Schall, 1892); methyl magnesium sulphite (Szarvasy, 1897); methyl and ethyl sodiumsulphites and ethyl potassiumsulphite (Rosenheim and Liebknecht, 1898), which are distinguished from alkylsulphonates in at once decomposing with water into phenol or alcohol and pyrosulphite, and in being formed by the union of sulphur dioxide with metal alkoxide or ammonium alkoxide. Warlitz's potassium ethyl sulphite has been shown by Rosenheim and Liebknecht to be only potassium ethylsulphonate. The new salts are not decomposed by excess of sulphur dioxide; Rosenheim and Liebknecht, who found that they were, must have allowed moisture to enter their vessels.

52. "*Ethyl Ammonium Selenite and Non-existence of Amidoselenites (Selenosamates).*" By Edward Divers and Seihachi Hada.

Selenium dioxide and ammonia, dissolved together in well-cooled alcohol, in the absence of any water, form a new salt, ethyl ammonium selenite, soluble in alcohol, insoluble in ether, and at once decomposed by water into acid ammonium selenite and alcohol. The salt soon begins to decompose at the common temperature, selenium being one of the products. Hinsberg obtained, in 1890, what appears to have been ethyl hydrogen selenite and ethyl phenyl ammonium selenite.

When water is also present, the ammonia and selenium dioxide do not unite with the alcohol, but with the water to form the ammonium selenites, a fact known to Berzelius. Cameron and Macallan (1888), proceeding apparently in the way the authors have prepared ethyl ammonium selenite, obtained instead salts which they describe as being selenosamates, But Cameron and Macallan record no property of their selenosamates which can serve to distinguish them from the half-acid and three-fourths-acid ammonium selenites, except their chemical composition, which was determined by methods of doubtful accuracy. The authors, therefore, believe that Cameron and Macallan cannot have taken sufficient precautions to exclude all moisture in their experiments, and conclude that there is no reliable evidence for the existence of amidoselenites. Accordingly, selenious acid seems to form no compounds analogous to amido-, imido-, or nitrilo-sulphates, any more than it forms salts like alkylsulphonates or salts having the constitution of metal sulphites.

Incidentally the authors obtained, in the pure state, normal ammonium selenite, half-acid ammonium selenite, and three-fourths-acid ammonium selenite.

53. "*The Allotropic Modifications of Phosphorus.*" By D. L. Chapman, B.A.

From experiments performed by the author, the following conclusions have been drawn:—

(1). "Metallic" and red phosphorus are identical. This is proved by their similarity in appearance when viewed under the microscope. The alleged higher vapour tension of some varieties of red phosphorus is due to impurity, which on heating decomposes with formation of phosphorus vapour.

(2). The vapours of red and ordinary phosphorus are identical. The vapour density of ordinary phosphorus has been determined at the boiling-points of mercury and of sulphur, and agrees closely with the density calculated on the assumption that the molecule consists of four atoms, although the results obtained by Mitscherlich and by Deville and Troost at higher temperatures would scarcely lead one to suspect that this would be the case.

(3). Red phosphorus melts, forming ordinary phosphorus, under pressure at the melting-point of potassium iodide. This point on the pressure temperature diagram the author proposes to call the triple point of red phosphorus. Melted ordinary phosphorus thus becomes superfused red phosphorus, and superfused ordinary phosphorus becomes the superfused liquid of both varieties. At ordinary temperatures red phosphorus is stable and white phosphorus unstable. Phosphorus, therefore, appears to possess in a remarkable degree the property of remaining in an unstable condition.

54. "*On the Interaction of Mercurous and Mercuric Nitrites with the Nitrites of Silver and Sodium.*" By P. C. Ray, D.Sc.

(1). *Mercuric and sodium nitrites.* To the neutral solution of mercurous and mercuric nitrites, the products of the dissociation of mercurous nitrite (*Trans.*, 1897, lxxi., 340), sodium chloride is added to remove mercurous salts. The filtrate containing mercuric and sodium nitrites, and possibly a small quantity of sodium chloride, is allowed to evaporate spontaneously. In course of time, an orange-red crystalline deposit is formed, followed by iodine-like scales, and finally crystals of sodium nitrate. Sometimes sodium nitrate is the only substance obtained. Unless sodium chloride is present, the coloured compounds are not formed. Analysis seems to show that the formula of the coloured substances is $HgCl_2,2HgO,\frac{1}{2}H_2O$, but they lose no weight in a desiccator over sulphuric acid nor when kept at 100°, but if heated in a bulb tube a deposit of moisture is invariably noticed. Millon, Thummel, Volhard, and Haack have described very similar compounds with the formula $HgCl_2,2HgO$, but no mention is made of any hydrated modification.

(2). *Mercurous and silver nitrites.* To a hot solution of

mercurous nitrite (containing mercuric nitrite) solution of silver nitrite was added. There was no effervescence, but the liquid at once became cloudy, and was allowed to stand overnight. Next day a clear solution was obtained, having at the bottom a layer of dirty grey mercury, and above it a deposit of shining, minute crystals of silver.

Careful analyses showed that, not only was there no loss of nitrogen during the reaction, but that it remained entirely in the form of nitrite.

With dilute solutions no silver was precipitated. In the reaction between mercurous and sodium nitrites, the nitrogen remained as nitrite, the mercurous nitrite decomposing entirely into mercuric nitrite and mercury.

The true explanation of the reactions has yet to be found, and with this end in view the author intends to make further experiments with solutions of the nitrites in varying degrees of dilution.

(To be continued).

SOIRÉE OF THE ROYAL SOCIETY.

Wednesday, May 3, 1899.

LIST OF OBJECTS EXHIBITED BY SIR WILLIAM CROOKES, F.R.S., ILLUSTRATING HIS PHOTOGRAPHIC RESEARCHES ON PHOSPHORESCENT SPECTRA.

IT has long been known that certain substances enclosed in a vacuous glass bulb phosphoresce brightly when submitted to molecular bombardment from the negative pole of an induction coil. The ruby, emerald, diamond, alumina, yttria, samaria, and a large class of earthy oxides and sulphides, emit light under these circumstances. Examined in a spectroscope the light from some of these bodies gives an almost continuous spectrum, while that from others, such as alumina, yttria, and samaria, gives spectra of more or less sharp bands and lines. Since 1879 the author has been working on these phosphorescent spectra, chiefly in connection with the earths of the yttria group, and by chemical fractionation he has succeeded in separating from this group bodies whose phosphorescent spectra consist chiefly of single groups of lines, other groups being absent. For the last six years the research has been extended beyond the visible spectrum, and photographs of the ultra-violet portion of the spectra are now being taken with a spectrograph with a complete quartz train. Some of the results of this research are here exhibited.

A. Spectrograph with two quartz prisms, quartz lenses, and condensers for photographing the ultra-violet spectrum. The slit is of quartz, cut and polished according to the author's method described in the CHEMICAL NEWS, vol. lxxi., p. 175, April 11, 1895.

The prisms are made in two halves according to Cornu's plan; one half of each being right-handed and the other half left-handed. One of the lenses is also right-handed and the other left-handed. By this device the effect of double refraction is so completely neutralised that with a five-prism instrument it is impossible, under high magnifying power, to detect any duplication of the lines, although the resulting photographs of spectra can be measured to 0·01 $\mu\mu$.

The sensitive surface must be curved (CHEMICAL NEWS, vol. lxxii., p. 87, August 23, 1895; and vol. lxxiv., p. 259, November 27, 1896) and set at an angle to obtain good definition over the whole spectrum. In the present instrument, using the middle position showing the whole spectrum on a plate, the angle is 40°, and the curvature is 190 m.m. radius.

B. A diagram of the spectrograph to full size, showing the arrangement of prisms, lenses, and condenser, the curvature and angle of sensitive surface, together with the path of the rays. Celluloid films are used, glass not being sufficiently flexible.

C, Photographed spectra of an alloy composed of equal molecular weights of zinc, cadmium, tin, and mercury. This alloy has been chosen as giving a standard spectrum, the lines of which are accurately determined and sufficiently close together to leave no wide unoccupied gaps in the spectrum.

When photographing a metallic, gaseous, or phosphorescent spectrum the spectrum of this alloy is photographed on the same plate, the known lines partially overlapping the unknown lines, to facilitate the calculation of their wave-lengths.

D. Photographs of a group of lines high up in the ultra-violet region, characteristic of a new element associated with yttrium, and separated by long fractionation. To this element the name VICTORIUM has been given.

E. Enlarged spectrum of the Victorium group of lines.

Victoria is an earth characterised by a group of lines in the neighbourhood of λ3110. In chemical characters it differs from yttria in many respects. From a hot nitric acid solution Victorium oxalate precipitates before yttrium oxalate and after terbium oxalate. On fractional precipitation with potassium sulphate the double sulphate of Victorium and potassium is found to be less soluble than the corresponding yttrium salt, and more soluble than the double sulphates of potassium with the terbium and cerium groups. Victorium nitrate is a little more easily decomposed by heat than yttrium nitrate, but the difference is not sufficient to make this reaction a good means of separating Victorium and yttrium. Fusing the nitrates can, however, be employed advantageously to separate mixed Victoria and yttria from the bulk of their associated earths. Tested by its position in a series of earths obtained by fractional precipitation with dilute ammonia, Victoria is found to be less basic than yttria and more basic than most of the earths of the terbia group.

The atomic weight of Victorium is probably near 117. In the purest state in which it has yet been prepared Victoria is of a pale brown colour.

F. Diagram of the fractionation of the crude yttria earths, showing the pedigree of Victorium.

PHYSICAL SOCIETY.

Ordinary Meeting, April 21st, 1899.

Mr. T. H. BLAKESLEY, Vice-President, in the Chair.

A MATHEMATICAL paper on "*The Effect of a Solid Conducting Sphere in a Variable Magnetic Field on the Magnetic Induction at a Point outside*," was read by Mr. C. S. WHITEHEAD.

It is an investigation of the magnetic induction at a point outside a solid conducting sphere when magnetic disturbances are taking place in the dielectric envelope. An expression is given for the maximum value of the magnetic induction when the sphere becomes an infinite plate and the inducing system consists of an alternating current in a circular circuit whose plane is parallel to the plate, *i.e.*, when the maximum value of the induction tangential to the surface is zero. A second expression gives the maximum value of the magnetic induction normal to the surface for a point at considerable distance from the axis, and just outside the plate. In this latter case, the maximum value of the induction tangential to the surface appears as a function of the maximum current of known frequency in the inducing circuit, the various dimensions in space of the system, and the permeability and specific resistance of the plate. From these equations, taking the most authentic values of the involved constants, the maximum magnetic induction normal to the surface for a sea-water plate is forty-four times as great as it would be for an iron plate, and more than three thousand times as great as it would be for a copper plate. The paper also shows that, for the purpose of induction telegraphy, to get the best effect the receiving coil should have its plane vertical—not horizontal; firstly, because the distance of the in-

ducing circuit from the surface of the plate must in practice be small compared with the distance of the point from the axis, so that the maximum normal induction is small compared with the maximum tangential induction; and secondly, because the maximum *normal* induction varies inversely as the *fifth* power of the distance of the point from the axis, whereas the maximum tangential induction varies inversely as the fourth power of that distance. In conclusion, Mr. Whitehead applies his formulæ to the practical case mentioned by Prof. Lodge in the *Journal of the Inst. of Electrical Engineers* (Feb., 1899, p. 805). Prof. Lodge there describes a horizontal receiving circuit, and states that, with no condensers in the circuit, he "was not usually able to hear anything" in the telephone. Mr. Whitehead calculates that under such conditions the theoretical value of the current in Prof. Lodge's horizontal secondary is 0·066 *micro*-ampères, but that with a vertical circuit the received current would have been 33 *milli*-ampères.

Mr. Blakesley observed that, as a rule, experiment preceded theory. He congratulated Mr. Whitehead upon having settled from theoretical considerations that the vertical position of the receiving coil is best.

Prof. Everett said that the very elaborate method of analysis adopted in the paper appeared to be very clearly stated. He would like to know whether the inducing coil ought to be vertical as well as the receiving coil.

Mr. Appleyard thought that experiment had left no doubt as to the best position of both coils. The early investigations of Mr. Willoughby Smith and the later work of Mr. H. R. Kempe and Mr. Preece had proved that for the best effect both coils should be vertical. But large vertical coils were difficult to fix and expensive to maintain. It was this reason probably that led Prof. Lodge to try what could be done with coils placed horizontally.

Mr. Whitehead, in reply, said that his formulæ only applied to a horizontal inducing coil. He had not worked out the case of what would happen if the inducing coil itself was vertical. In the Flat Holm experiments both circuits were straight wires with their ends to earth, so that they really amounted to vertical coils.

Mr. R. A. Lehfeldt then gave a demonstration of a method due to Prof. T. W. Richards for standardising thermometers. This depends upon the ordinary latent-heat principle for maintaining constant temperature, but it includes the consideration of generally more than two states or phases of the melting substance. If there are c components and p phases, then the number of degrees of freedom of the system is $[c+2-p]$. When this is zero, the temperature and the pressure of the system are perfectly definite. Thus the following chemical formula represents the four phases to be equilibrated in the case of Glauber's salt:—

$$\left\{\begin{array}{l} Na_2SO_4 10H_2O \\ Na_2SO_4 \\ \text{Solution} \\ \text{Vapour.} \end{array}\right.$$

Prof. Richards has determined the temperature of equilibrium in several useful cases. The salts are put into a test-tube in an air-bath formed between it and a second test-tube; the whole is then heated in a beaker of water over a small flame. If the salt is pure, and care is taken to avoid the effect of supersaturation, this method is highly satisfactory. It gives an extensive range of fixed-points, and is especially useful in thermometry for fixed-points between 0° and 100°. A few of these temperatures may be noted:—

Sodium chromate	19·71° C.
Sodium carbonate	53·3
Sodium thiosulphate ..	48·0
Sodium bromide	50·8
Manganese chloride ..	57 8
Trisodium phosphate ..	73·4
Barium hydroxide	78·0

Mr. J. A. Harker asked how long the temperature remained constant. The special value of Richards's method for standardising thermometers of short range had been pointed out by Dr. Chree. It obviated the necessity for auxiliary bulbs, and it would be extremely useful in graduating meteorological thermometers.

Mr. Blakesley said that sodium chromate was represented by a very useful temperature. Could this substance be regarded as sufficiently stable to give a satisfactory fixed-point?

Mr. Lehfeldt, in reply, said that the time taken by the transformation was certainly several hours. All the fixed points mentioned were theoretically as definite as that corresponding to sodium sulphate, but they had not been so accurately determined.

NOTICES OF BOOKS.

Precious Stones and Gems: their History, Sources, and Characteristics. By Edwin Streeter, F.R.G.S., M.A.I., Gold Medallist of the Royal Order of Frederic, Holder of a Gold Medal from H.M. the King of the Belgians. Sixth Edition, Revised, and largely Re-written, up to date. London: George Bell and Sons, York Street, Covent Garden. 1898.

This beautifully illustrated volume is probably the most complete treatise that has yet appeared on the subject of precious stones. The present issue has been subject to revision, and contains the latest information on the history and properties of gems. From an author whose enthusiasm is so well known it could not fail to be both interesting and valuable. In his preface the author points out that the science of gems must necessarily include a competent knowledge of crystallography, physics, chemistry, and geology, but there are for the identification of precious stones several simple but valuable means which admit of application without any profound knowledge of mineralogy, and these tests have been included in an Appendix at the end of the book.

The need on the part of the jeweller of a sound knowledge of the properties of gems is amply illustrated by the following incident:—Some family jewels, consisting of a sapphire and diamond suite that had passed the probate several times, and had been valued by one of the first jewellers of the day, were handed to the author to report upon, and after examination he had the unpleasant duty of informing the unfortunate legatee that the *sapphires* were only paste! Had they been genuine they would have been worth from £30,000 to £40,000.

A considerable section of the book is naturally occupied with the history and properties of the diamond, and includes some interesting and little-known facts. In the early days of the present African mines, when much scepticism was abroad as to the genuineness of the mines, Mr. Streeter cleared up the doubts of many by sending out a representative, who not only purchased and reported upon the stones, but also acquired considerable interest in the workings. It is remarkable that public recognition of South African diamonds was so long withheld, although it appears certain that the presence of diamonds was known to European colonists as early as the middle of last century. In a mission map, dated 1750, the words "here be diamonds" are to be seen inscribed across the territory of Gricqualand West. The old Dutch residents of Cape Town were also well acquainted with the fact, but very little was heard about the matter until about thirty years ago, when chance brought to light, at a farm near Cape Town, a very fine crystal, which ultimately found its way to the Paris Exhibition, and so public attention was directed to the matter.

Of all the popular errors that have surrounded the diamond, one of the most astonishing—because it has

hardly disappeared even at the present day—is that it cannot be broken by a hammer! Through this ignorance many a fine crystal has been lost. Pliny, in an account of the diamond, asserts "that the superiority over fire and steel is subdued by goats' blood, in which it must be soaked while fresh and warm, and then only when the hammer is wielded with such force as to break both it and the anvil will it yield."

Passing on to historical diamonds, drawings are given of the famous Koh-i-nur both before and after re-cutting; it is remarked that the ancients did not appreciate the art of the lapidary so highly as we do, and would have been horrified at sacrificing 80 carats of a stone weighing 186 carats, as in the re-cutting of the Koh-i-nur, and one cannot help thinking that the horror is not exclusively confined to the ancients. In many quarters the wisdom of converting the famous "mountain of light" into a modern brilliant of less than two-thirds its original weight has been questioned.

A remarkable story is told of the Agra or Delhi diamond—a pink stone of very great beauty—and the manner of its transference to England. Certain young officers in the regiment at Delhi having obtained possession of the stone, determined to smuggle it home, and so escape sharing its value as loot. After many suggestions one of them hit on the bright idea of enclosing it in a horse ball, and causing one of the regimental horses to swallow it. Having reached the port of embarkation the innocent smuggler was "taken ill," and had to be shot, and the stone having been removed from its stomach was brought to England. It has since been re-cut, and its weight reduced from 46 carats to 31½.

The beautiful "Eugene" diamond that was sold for a very large sum to the Emperor Napoleon III. is recorded to have been first found by a poor Indian peasant, who offered it to the village blacksmith in return for repairing his plough. The blacksmith valued it so lightly as to fling it away, but afterwards, thinking better of it, picked it out of his rubbish heap, and ultimately succeeded in selling it for 6000 rupees!

Perhaps the most important of all coloured diamonds was the famous blue stone once the property of Louis XIV., which appears originally to have had the form of a large drop or pendant. During the troublous times of the Revolution in 1792 this gem vanished, and has never since been found; but in 1830 a very fine blue brilliant, of some 23 carats weight, came to light without a history. Subsequently a small blue drop-shaped stone, of identically the same colour, was purchased in Geneva, and finally a still smaller blue stone was bought in Paris by the author. These three stones exactly accounted for the lost gem.

Passing from historical diamonds, an account is given of the occurrence of minute diamonds in the meteorites of the Canyon Diablo in Arizona, first recognised by Mr. A. E. Foot, of Philadelphia, and since confirmed by many observers; and the theory that the diamond deposits or pipes of the Kimberley mines are of meteoric origin is discussed. The property of phosphorescence in the diamond is very marked; exposure to bright light for a few minutes causes some stones to shine brilliantly in the dark. The author mentions an instance of an orange-coloured stone which, after exposure to lime-light, became sufficiently luminous to light up a room. Reference is made to the beautiful property of diamonds, first pointed out by Sir William Crookes, of phosphorescing under molecular bombardment *in vacuo*, as well as the more recent observation of its great transparency to Röntgen radiation.

The section closes with a short description of the best-known African mines, and a full-sized drawing of the "Excelsior" diamond, of 970 carats weight, from the Jagersfontein mine, now in process of cutting at Amsterdam. A good description is given of the mines, and methods of working in India, Brazil, Borneo, Australia, and America. This last country is responsible for an attempted gigantic fraud. In the year 1870 large discoveries of diamonds were reported from Arizona; but it was eventually found that the ground had been "salted" with diamonds and other precious stones, purchased in England for that purpose!

In connection with the ruby mines of Burma, the author tells a story that shows in strong relief the energy and perseverance necessary to carry on an enterprise of this kind, and, in spite of the disappointing results that seem to have attended the operations of the present ruby mines, hopes are held out of better things in the future.

There are few gems more associated with romance and superstition than the opal. As described by Nichols, two and a half centuries ago, "The opal is a precious stone which hath in it the bright fiery flame of the carbuncle, the fine refulgent purple of an amethyst, and a whole sea of the emerald's green glory; and every one of them shining with an incredible mixture and very much pleasure." Pliny describes an opal valued at £20,000 of our money, the property of Senator Norius, who was proscribed by Marc Antony for the sake of this gem, but, making his escape, carried it with him as the sole relic of his fortune, preferring exile with his opal to life in Rome without it.

In connection with agates it is mentioned that very fine coloured ones are produced by the method of dyeing, *i. e.*, steeping the stones in various metallic solutions and then heating: one process is to soak the stones in an aqueous solution of honey and afterwards in sulphuric acid, and, finally, strongly heating, whereby the volatile products are removed and carbon deposited in the porous parts of the stone, producing many fine effects.

The illustrations given in the volume are very good, both for mineralogical accuracy and beauty; and at the end of the book there is a classification of precious and semi-precious stones under seven separate heads, according to their chemical composition. This cannot fail to be of value to any one interested in precious stones, whether as amateur or professional.

OBITUARY.

PROFESSOR C. FRIEDEL.

We regret to announce the death of M. Charles Friedel, Dean of the Chemical Section of the French Académie who died at Montauban, after a very short illness, on Wednesday, April 19th, at the age of sixty-seven.

At the meeting of the Académie on April 24th, the President referred to their recent loss in the following terms:—

M. Friedel was a pupil of Würtz, whom he succeeded in the Chair of Organic Chemistry at the University of Paris. All his efforts were devoted to continuing and developing the work of his illustrious master and friend. By his numerous and important researches, which opened the doors of the Académie to him in 1878, and by the distinguished pupils which were trained in his laboratory, he exercised a great influence on the progress of organic chemistry in France throughout the last quarter of a century. It would be well for others to follow, one by one, all the stages of this active scientific life.

This sudden and unexpected departure of our colleague will be nowhere felt more than in our Académie, where we have appreciated—above all, in that it extended scientific research—the amiability of his person and the uprightness of his character, indefatigably upholding justice and truth.

In the assurance that I am interpreting the sentiments of all, in rendering to him this last homage, I close this meeting as a sign of mourning.

CORRESPONDENCE.

LABORATORY GAS FURNACE.

To the Editor of the Chemical News.

Sir,—Our attention has been drawn to a note in the Chemical News of March 17th (vol. lxxix., p. 131) stating that the Holloway Patent Furnace—of which we are makers, and of which you gave a notice on September 23rd, 1898, p. 157—is "almost identical with one that Messrs. Fletcher, Russell, and Co. inform us has been made by them for the last fifteen or twenty years." With this we cannot agree. The shape and size are practically identical—because they are the most convenient, and could not well be different—but the construction is entirely new.

The Holloway furnace body is made in two parts, which increases its portability and renders it cheaper and less liable to crack. The base extends forward and forms a table in front of the furnace; the body has no side flanges extending beyond the base or top, so that the doors cannot get jammed. The deep flanges on the doors prevent them from falling down; and the burner is of a new construction. All these features add to the value and convenience of the furnace very considerably, and render it entirely different to previous forms.—We are, &c.,

John J. Griffin & Sons, Lim.

20—26, Sardinia Street, Lincoln's Inn Fields,
London, April 26, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 15, April 10, 1899.

New Method of Preparation of Iron Silicide, SiFe.—P. Lebeau.—The author employs silicide of copper as a solvent for silicide of iron, which allows of the preparation of the compound SiFe in a well crystalline form. He also proves that at a high temperature copper silicide dissociates, and is capable of yielding its silicon to another metal, such as iron, which has a greater affinity for silicon than the original copper. This reaction can be applied to the preparation of other metallic silicides; the author having verified the reaction in the case of the silicides of cobalt, nickel, and chromium. The employment of the arsenides and stibnides of copper has led to comparable results. The author proposes to continue the investigation of these binary compounds by this new method.

Preparation and Properties of a Crystalline Subphosphide of Copper.—Georges Maronneau.—M. Moissan showed that, by the reduction of calcium phosphate by carbon in the electric furnace, crystalline phosphide was obtained. The author extends this method to the preparation of other phosphides. By the reduction of copper phosphate by carbon in the electric furnace, he obtains a phosphide of copper in a crystalline form, having the formula Cu_2P. This compound has density 6·4. When heated in a current of hydrogen to a temperature of 1000°, the phosphide loses a small quantity of phosphorus, and becomes a grey powder; it is attacked slowly by acids in the cold, except nitric acid; it is completely soluble in hot nitric acid. Heated slightly in oxygen, it oxidises. In the presence of fusing sulphur, formation of copper sulphide takes place with incandescence.

Thermic Properties of Lime Prepared at Different Temperatures.—Henri Gautier.—The rapidity of hydration of lime varies considerably with the conditions of temperature at which it is obtained. Lime prepared at 1000°, thrown into a large quantity of water, unites so rapidly as to vaporise some of the water; when prepared at 1300°, it is attacked quietly; and extremely slowly if prepared at a much higher temperature in the electric furnace. The author has investigated these reactions, to find whether these differences in the rapidity of hydration are due to a difference in the molecular state of the chalk when prepared at different temperatures. He used pure lime prepared by the calcination of Iceland spar. His results show that the amount of heat developed is the same in all cases.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., June 27, 1898.

On the Heat of Volatilisation of some Elements, and on their Molecular Weight in the Liquid State.—J. Traube.—The formula given by Clausius,—

$$\rho = T \frac{dp}{dT} (v_1 - v_2),$$

in which ρ is the latent heat of volatilisation, T the boiling-point in absolute degrees, v_1 and v_2 the specific volumes of the vapour and of the liquid at the temperature T, enables us to calculate, after integration, the molecular weight in the liquid state. By applying this equation we find that the elements Br, I, Zn, Cd, Hg, and Bi have the same molecular weights in the liquid and gaseous states (Zn, Cd, Hg, and Bi are monatomic, Br and I are diatomic). Sulphur is an exception. The above formula can be replaced by that of Trouton, of which it is the definite integral at the normal pressure, $\frac{m\rho}{T} = 20{\cdot}63$. The values of ρ given by this last equation do not coincide with those furnished by the first formula except when the elements have the same molecular complexity in the liquid and gaseous states.

Spectro-chemistry of Nitrogen (continued).—J. W. Brühl.—Nitrosobenzene gives optical constants leading to the double formula $C_6H_5{-}N{-}O$ / $O{-}N{-}C_6H_5$. Nitrosochloride of tetramethylethylene has similar anomalies, and should have one of the following constitutions:—$(CH_3)_2.C{-}C(CH_3)_2$ / $N.OCl$ or $(CH_3)_2.C{-}C.(CH_3)_2$ / $ClN{-}O$. Phenylhydroxylamine has the generally accepted formula C_6H_5NHOH. The oxygenated ethers of dinitrobenzene have an abnormal refraction. Nitrourethane should be classed among the nitramides, and have the constitution

$$C_2H_5OCO.NH{-}N\langle{}^{O}_{O}$$

Some Double Glycerolates of Copper and the Alkaline Metals.—F. Bullheimer.—Glycerolate of copper and sodium, $(C_3H_5O_3CuNa)_2 + C_2H_5OH + 9H_2O$, is obtained by two methods:—By the first way, we dissolve 5 grms. of cupric hydrate in 3 grms. of glycerin containing 3 grms. of NaOH and 15 c.c. of water; we then add 50 c.c. of alcohol, filter, and add more alcohol until the cloudiness is persistent. By the second method, 150 c.c. of an alcoholic solution of acetate of copper saturated at 60°, are added to 50 c.c. of water, 6 grms. of glycerin, and 100 c.c. of ethylate of soda (containing 5 grms. of Na); add 100 c.c. of alcohol, and allow to cool. We thus obtain blue prismatic needles, which lose their alcohol and part of their water (6 mols.) *in vacuo*. The methods of preparing the glycerolates $C_3H_5O_3CuNa.3H_2O$ and $C_3H_5O_3CuLi.6H_2O$ are also described. These two products crystallise in hexagonal blue tables.

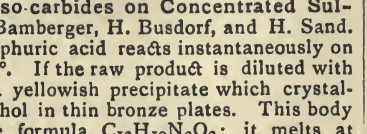
New Oxidation Product of Theobromine.—H. Clemm.—The oxidation of theobromine by means of HCl and $KClO_3$ gives an oxydimethyluric-3.7 acid, analogous to the oxy-β-dimethyluric acid obtained by Fischer by oxidising β-dimethyluric acid by the same process. Oxydimethyluric acid crystallises in the form of thin plates, fusible with decomposition at about 201—203°, slightly soluble in water and the cold organic solvents, also in the alkalis. Boiling baryta-water splits this acid up into mesoxalic acid and methylurea.

Action of Nitroso-carbides on Concentrated Sulphuric Acid.—E. Bamberger, H. Busdorf, and H. Sand.—Concentrated sulphuric acid reacts instantaneously on nitrosobenzene at 0°. If the raw product is diluted with water, we obtain a yellowish precipitate which crystallises in boiling alcohol in thin bronze plates. This body corresponds to the formula $C_{12}H_{10}N_2O_2$; it melts at about 152°, decomposing brusquely, and dissolves easily in chloroform and warm acetone; it is slightly soluble in benzene, ether, and ligroin, and insoluble in water. Reducing agents transform it into *p*-aminodiphenylamine. The authors have also given it the formula of a *p*-nitrosodiphenylhydroxylamine, $C_6H_5.N(OH).C_6H_5.NO$. Several derivatives are described, such as the monacetyl, the *p*-nitroso-di-*o*-tolylhydroxylamine, &c.

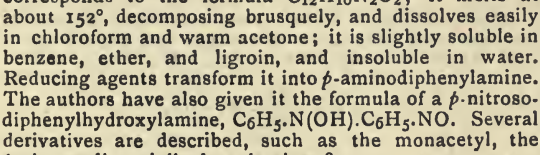
Action of Phenylhydroxylamine on Aniline and on Sulphuric Acid in the presence of Alcohol.—E. Bamberger and Jan. Lagutt.—When we heat a mixture of phenylhydroxylamine (100 grms.), absolute alcohol (2400), and sulphuric acid (50 c.c.) for twenty-four hours on a water-bath, we obtain the following products:—Nitroxybenzene (14 grms.), *p*-phenetidine (45·8 grms.), *o*-phenetidine (8 grms.), *p*-aminophenol (3·5 grms.), *o*-aminophenol (3·5 grms.), aniline (4 grms.), nitrophenol, phenol, &c. (traces). In the cold we only obtain nitroxybenzene, aniline, and *p*-amino-phenol. In no case were the authors able to isolate the compound $C_6H_5.NH.OC_2H_5$. The authors have also studied the action of aniline on phenylhydroxylamine. A solution of 75 grms. of phenylhydroxylamine in 100 grms. of aniline, was gradually added to a solution of hydrochlorate of aniline (105 grms.) in 130 grms. of aniline heated to 130°. At the end of one hour the phenylhydroxylamine had disappeared and the mass contained the following products:—Nitroxybenzene (17 grms.), various colouring-matters (19 grms.), sulphate of benzinidine (10 grms.), sulphate of *p*-aminodiphenylamine (8·6 grms.), *o*-aminodiphenylamine (6·4 grms.), chloraniline (traces). In another experiment, *p*-aminophenol was also obtained.

Derivatives of Tetrahydropyrone.—P. Petrenko-Kritschenko.—The aromatic aldehydes react easily on ether or acetone dicarbonic acid, giving rise to very slightly stable intermediate products, which themselves lose carbonic acid while being transformed into tetrahydropyrone derivatives:—

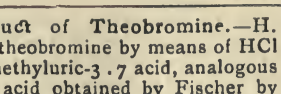
$$CO_2H.CH_2.CO.CH_2.CO_2H + 2R.CHO =$$



$$+ H_2O.$$



The stability of these pyronic derivatives is very variable. Dimethoxydiphenyltetrahydropyrone,—



is obtained by saturating a mixture of acetone dicarbonic acid (1 mol.), methylsalicylic aldehyde, and acetic acid with hydrochloric acid gas. The product is dissolved in Na_2CO_3 and precipitated with HCl. We thus obtain the corresponding dicarbonic acid which loses CO_2 at the temperature of the water-bath.

MISCELLANEOUS.

Drown's Method of Determining Silicon.—A. C. Langmuir.—In the July number of the *Journal of the American Chemical Society*, George Auchy has described a method devised by him, which will effect a more thorough dehydration of the silica than is obtained by the method usually followed. Dr. Dudley (*Journ. Amer. Chem. Soc.*, xix., 106) called attention to the difficulty of dehydrating in this case at the Troy meeting of this Society in 1896. Without claiming any superiority over Mr. Auchy's method, it may be of interest to describe a modification which has been in use in this laboratory for a number of years. It is not original with the author. The pig iron or steel is weighed into a No. 4 beaker, and brought into solution by the usual method as described by Blair. We then add 40 c.c. of concentrated sulphuric acid, and evaporate to fumes on the hot plate. A leather strap, about 1 inch broad and 20 inches long, is passed under the lip of the beaker, and the ends clasped between the thumb and forefinger. By a slight wrist movement the contents of the beaker are given a rapid rotary movement. The beaker can, in this way, be heated directly in the full flame of the Bunsen burner with perfect safety. Care only must be taken that the contents are kept in continual motion, and that sufficient acid is present to cover the glass exposed to the flame. Under these circumstances any lumps are broken up, and a thorough contact between the silica and the very hot acid is insured. In many other cases where evaporation to fumes is necessary, and the tendency to bump prevents the simple boiling down of the solution, the use of a strap in this way is invaluable. As a rule it will be found more convenient than the use of the casserole. It is also very convenient in handling hot beakers, as it is adaptable to one of any size. We perhaps run the risk of recounting what may be to some chemists an old story, but, as in our experience we have yet to visit a laboratory in which the strap was used in this way, it is but reasonable to conclude that it has not met with the attention it deserves.—*Journ. Amer. Chem. Soc.*, xxi., No. 2.

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Society of Arts, 8 (Cantor Lectures). "Leather Manufacture," Prof H. R. Procter, F.I.C.
—— Royal Institution, 5. General Monthly Meeting.

TUESDAY, 9th.—Royal Institution, 3. (The Tyndall Lectures). "Electric Eddy-currents," by Prof. Silvanus P. Thompson, D.Sc., F.R.S.

WEDNESDAY, 10th.—Society of Arts, 8. "Fruit Growing in Kent," by George Bunyard.

THURSDAY, 11th.—Royal Institution, 3. "Embroidery," by Lewis F. Day.
—— Society of Arts, 4.30. (Indian Section). "Agrarian Conditions under British and Native Rule," by Michael Francis O'Dwyer, I.C.S.

FRIDAY, 12th.—Royal Institution, 9. "Magnetic Perturbations of the Spectral Lines," by Prof. Thomas Preston, M.A., D.Sc., F.R.S.

SATURDAY, 13th.—Royal Institution, 3. "To Iceland in Search of Health" (with Lantern Illustrations), by W. L. Brown, L.R.C.P., L.R.C.S.

THE CHEMICAL NEWS.

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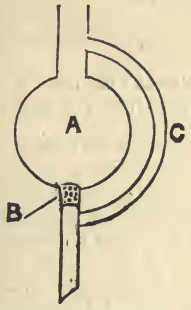
ON SOME NEW APPARATUS.

By F. W. ASTON.

Having occasion to prepare large quantities of pyromucic chloride for some research in which I am at present engaged in conjunction with Prof. P. F. Frankland, new forms of apparatus were devised, and, as they may be of some service to other experimenters, they are here described.

I. *A Chlorinating Apparatus.*

Owing to the comparative insolubility of pyromucic acid in chloroform, its reaction with PCl_5 in this solution, using the ordinary apparatus, is very inconvenient. The following apparatus, however, avoids all choking of the condenser, works automatically, and at the same time allows of the use of crude acid.



The apparatus is made of glass, and is of the simple form shown in the accompanying sketch. The crude acid is placed in the bulb A, being prevented from falling out by a plug of glass-wool, B. A flask, containing the PCl_5 and chloroform, is attached to the lower extremity, and a reflux condenser is fitted to the upper. On boiling the contents of the flask on a water-bath, the chloroform distils up the side tube C, and, being condensed, flows back through the bulb into the flask, drop by drop, saturated with acid, being freed from all tarry and other insoluble matter by the glass-wool; here it reacts with the PCl_5 in the usual manner.

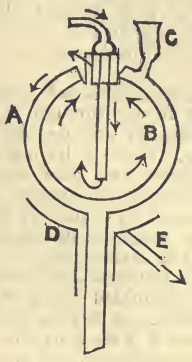
By means of this arrangement the reaction is rendered perfectly smooth, and needs practically no attention when once set at work.

II. *New Form of Condenser.*

With the above apparatus I have used a new form of double surface condenser, very suitable on occasions where a reflux condenser is required, and possessing advantages over condensers previously described by reason of its great efficiency. It is made of glass, in the form shown in the accompanying sectional sketch.

It consists of an outer bulb, A, from a thickened part of which is formed by suction a very thin concentric inner bulb, B, through which the cooling water circulates as indicated by the arrows, subsequently flowing in a thin stream over the outer surface of the bulb A into the cup D, and running to waste through the escape tube E.

The spherical shape of the condenser and its peculiar method of construction enable the inner bulb to be made of exceedingly thin glass, without fear of breakage and render the effective cooling surface enormously great compared with the space occupied. As the side tube C is joined on at the thickest part of the bulb, the structure is rendered very strong and rigid.



For reflux work it is most convenient to have the side tube pointing upwards, as in the figure, but if it is fused on at an angle the condenser can be used for ordinary distillations, and has the advantage of taking up very little bench space.

Mason University College, Birmingham.
April 28, 1899.

ON THE PRODUCTION OF CRYSTALLISED TUNGSTEN BY ELECTROLYSIS.

By L. A. HALLOPEAU.

I have already shown, in previous papers, the reducing action of hydrogen and tin on melted paratungstate of lithium.

Tin reacts on this salt, giving a tungstolithic tungstate. With hydrogen the reduction is more complete; we obtain at a red heat crystallised binoxide of tungsten, which at a higher temperature would be itself reduced to the metallic state.

Following up these experiments, there remained to study the action of electrolysis on melted tungstate of lithium. The electrolysis of the paratungstates of sodium and potassium gives rise to alkaline tungsto-tungstates; with the lithium salt the result is different.

Paratungstate of lithium, melted in a porcelain crucible and carried to a temperature of about 1000°, was submitted for three hours to the action of an electric current of 3 ampères and 15 volts; the electrodes were of platinum. The melted mass was treated successively with boiling water, concentrated hydrochloric acid, and a boiling solution of lithia at about 20 per cent; after a final washing with warm water there remains a distinctly crystalline substance. This is tungsten mixed with a certain amount (up to 6 per cent) of platinum; the platinum comes from the electrodes which are attacked by the melted lithia.

Tungsten thus obtained is in the form of opaque crystals, having a beautiful metallic lustre and a prismatic appearance. As a rule these crystals take the form of needles, which have some resemblance to the needles of silicon; they might very well be piled up octahedra, as is the case with silicon.

To analyse this substance it suffices to submit it to the action of a current of oxygen at a red heat, so as to burn all the tungsten, which is transformed into tungstic acid. The product of the oxidation is then melted with carbonate of soda. The melted mass is re-dissolved in water, and filtered to separate the platinum; in the filtrate the tungstate acid is precipitated in the form of

mercurous tungstate. As a check, the increase in weight resulting from the oxidation of the material in the current of oxygen should be equal to the theoretical weight of the oxygen necessary to transform the tungsten present into tungstic acid. This method allows of the rapid analysis of all the products of reduction of the acid tungstates, oxides of tungsten, and alkaline tungsto-tungstates.

Zettnow has already obtained metallic tungsten by passing an electric current through melted tungstate of sodium, but the tungsten prepared by this method was black and powdery. Most of the methods tried for the preparation of tungsten also give amorphous products. Wöhler's method, which consists of reducing the acid tungstate of potassium by a current of hydrogen, alone furnishes crystalline tungsten: by the aid of a very powerful glass I was able to distinguish, in the midst of these crystalline grains, a few crystals in the form of needles, which very closely resembled those of the tungsten obtained by the electrolysis of the paratungstate of lithium.

I have not succeeded in electrolysing the paratungstate of lithium with iron electrodes, this metal being attacked very readily by the melted salt. I propose repeating the experiment, using iridio-platinum electrodes. In any case the electrolysis of the paratungstate of lithium only enables us to obtain very small proportions of the metal; the only method by which large quantities can be obtained is that of M. Moissan, who has shown that, with the help of the electric furnace, we can prepare melted tungsten in a state of absolute purity.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 24.

HYPERBORATES AND HYPERTITANATES.

By P. MELIKOFF and L. PISSARJEWSKI.

HYPERBORATE of ammonium, $NH_4BoO_3+\frac{1}{2}H_2O$, is prepared by dissolving boric acid in an aqueous solution of peroxide of hydrogen at 2·5 per cent, adding ammonia, and precipitating the salt with alcohol. This salt occurs in white crystals, very stable when dry. In the same manner as hyperborate of soda, already described (*Berichte*, xxxi. [4], 678), it gives off peroxide of hydrogen when treated with dilute sulphuric acid, ozone when treated with concentrated sulphuric acid, and chlorine when treated with hydrochloric acid. It dissociates in aqueous solution at the ordinary temperature, but more rapidly at 45° C., giving off oxygen and forming nitrate of ammonia. The freshly precipitated salt contains 3 molecules of water of crystallisation, but after having been kept over sulphuric acid for twenty-four hours it only retains half a molecule.

The barium salt, $Ba(BoO_3)_2+7H_2O$, is prepared by the double decomposition between a saturated solution of the soda salt at 0° C. and a solution of chloride of barium. It is difficultly soluble in water, and behaves like the ammonium salt when treated with acids. It decomposes slowly at the ordinary temperature.

The calcium salt, obtained in an analogous manner, is much less stable in water than the barium salt, and it is equally insoluble.

The insoluble hyperborates of nickel and of copper, obtained by the action of the sulphates of these metals on the soda salt, decompose rapidly with the evolution of oxygen. It is due to this circumstance that their analysis has not been effected.

By the action of chloride of cobalt on hyperborate of soda, we obtain the peroxide CoO_2,CoO, with evolution of oxygen. The salts of manganese give an analogous reaction.

Every attempt to obtain compounds of hyperboric acid with the metallic peroxides has been unsuccessful.

Hypertitanic acid forms, with the metallic peroxides, not only basic salts of the type $(R_2O_2)_2TiO_3$, but also neutral salts of the type $R_2O_2.TiO_3$.

Hypertitanate of normal peroxide of sodium, $(Na_2O_2.TiO_3+3H_2O)$, is obtained either by the action of peroxide of hydrogen and caustic soda on titanic acid, and the decomposition of the solution by alcohol, or else by the decomposition of the basic salt by means of water. In one and the other case a thick oily liquid separates, which changes into a yellow powder by desiccation over sulphuric acid. Treated with dilute sulphuric acid, this salt gives off peroxide of hydrogen; it also decomposes hydrochloric acid with the liberation of chlorine.

The hypertitanate of peroxide of ammonium, $(NH_4)_2TiO_3.H_2O_2$, is prepared by pouring a solution of peroxide of hydrogen over hypertitanic acid, adding ammonia and precipitating the salt by alcohol. This salt crystallises in small yellow prisms. It is fairly stable in the dry state, but dissociates in aqueous solution with the evolution of oxygen. It detonates slightly when heated over a flame. Dilute sulphuric acid and hydrochloric acid act on it as on the soda salt.

The hypertitanate of the normal peroxide of barium, $BaO_2.TiO_3+5H_2O$, is prepared by double decomposition between the soda salt and chloride of barium. Dried over sulphuric acid it appears as a yellow powder.—*Berichte*, xxxi. [7], p. 953.

A NEW HYDRATE OF THE SALINE OXIDE OF CHROMIUM.

By G. BAUGÉ.

THE various double carbonates of protoxide of chromium, of which we have already described the preparation and properties, all gave the same reaction with boiling water. All the carbonates, in fact, when treated with boiling water and protected from contact with the air, gave a hydrated oxide of chromium which was shown by analysis to be a saline oxide containing 3 molecules of water.

Peligot (*Ann. Chim. Phys.*, Series 3, vol. xii., p. 539) has already shown the existence of a hydrate of the saline oxide containing 1 molecule of water. The hydrate I have obtained is thus different to that which has been described by Peligot. I therefore propose to describe its preparation and properties.

Preparation.—We used the same apparatus that served for the preparation of the double salt of sodium, but replacing the tubulated flask with a flask closed with a cork giving passage to two easily fitting tubes bent at right angles. This apparatus was traversed by a current of carbonic acid free from oxygen, a certain quantity of one of the double salts of protoxide of chromium* was placed in the flask; then, by means of the tubes, boiling water was poured on to the product, and the boiling kept up for about half an hour. Directly the water is added the salt decomposes, losing carbonic acid and hydrogen; but it is important, for the rapid termination of the reaction, to boil for some time, as mentioned above. The mixture is then passed, while still agitating, to the filtering-tube which terminates the apparatus; then, with the aid of a filter-pump, we wash the product with boiling water until the washings are no longer precipitated by chloride of barium.

In this manner we obtain a brick-red body, which is dried at 100° in the tube itself. During this desiccation we notice that this body changes colour, and becomes yellowish brown while losing water. This transforma-

* The best results were obtained with the double salt of potassium. We can even proceed without first preparing the double salt; it suffices to have in the flask the necessary ingredients for making this salt.

tion occurs gradually in the direction of the entrance of the current of gas, and the surface of the separation of the two layers is quite distinct.

If the separation is stopped before the completion of this change, we can, after cooling, remove from the immediate neighbourhood of the surface of separation portions of the brick-red body.*

Analyses made on samples from several experiments cause us to believe that this unstable brick-red body is a hydrate of the saline oxide, containing 4 molecules of water.

The Yellow-brown Hydrate. — This substance can be most rapidly obtained by closing one end of the tube containing the brick-red body, placing it in boiling water, and making a vacuum by the other end, until it no longer loses water.

Properties.—This hydrate cannot be confounded with the former one. In fact, if it is placed in the presence of boiled water, in an inert atmosphere, it remains a yellow-brown. Further, even after a month, it does not regain the water of hydration which it lost. It occurs in the form of a yellow-brown powder, with a density of 3·49. Heated *in vacuo*, in a current of steam, hydrochloric acid gas, or an inert gas, it gives, at about 250°, sesquioxide of chromium with a loss of hydrogen, but without incandescence.

It is attacked by chlorine at a dull red heat with the evolution of steam, subchloride of chromium, and hydrochloric acid gas: this class of reaction has already been noted by M. Moissan. Though fairly stable in dry air, it oxidises rapidly in the presence of water. This oxidation is the more lively as the compound has been the more recently prepared. Heated in air, it then gives sesquioxide of chromium without incandescence. Sulphuretted hydrogen below a red heat transforms it into a crystallised sulphide. It is an energetic reducing agent. When placed in contact with dilute sulphuric acid it reduces it at about +40°. This reduction may go on to the formation of sulphuretted hydrogen if the oxide is added in sufficient quantity..

Treated warm with concentrated hydrochloric acid it gives a mixture of chromous and chromic chlorides. The formation of the chromous salt may be shown in the following manner:—We place anhydrous sesquichloride of chromium and concentrated hydrochloric acid in a tube traversed by a current of carbonic acid, and boil; no solution takes place. If we now add a small quantity of the saline oxide, the sesquichloride goes rapidly into solution. We know that this solution is characteristic of the salt of protoxide of chromium. All efforts to effect complete dehydration without decomposition, or to obtain Peligot's hydrate, have given no results.

Analysis.—We used the method described by Peligot (*loc. cit.*).

The water given off by a known weight of oxide when heated in a current of dry carbonic acid is weighed; we also weigh the residue, and measure the volume of hydrogen arising from the water decomposed by the oxidation of the protoxide. This method of analysis gives, in a single operation, all the elements required for the calculation. The hydrogen shows, on the one hand, the weight of oxygen necessary to cause the oxide under examination to pass to the state of sesquioxide; on the other hand, the quantity of water which corresponds to it, and which, added to that collected in the tube, gives everything constituting the hydrate, and, subtracted from the weight of the material used, gives the weight of the anhydrous oxide. The weight of the sesquioxide formed controls the preceding results.

This method has given us the following results, expressed in parts per cent:—

	H_2O collected and weighed.	H collected at 0° and 760 m.m.	Residue, calculated as chromium.
I.	16·55	4075·7 c.c	56·65
II.	16·08	4063·4 ,,	57·19
III.	16·32	4057·7 ,,	56·42
Theory	16·42	4064·5 ,,	56·93

The brick-red compound gave us the following quantities of water:—

I.	II.	III.	Theory.
21·96	22·07	21·12	21·57

To sum up, the saline oxide of chromium is susceptible of several states of hydration:—

1. $CrCr_3O_4.H_2O$, obtained by Peligot.
2. $CrCr_3O_4.3H_2O$, determined by us.
3. A brick-red unstable hydrate, which analysis enables us to consider as containing 4 molecules of water.—*Bull. Soc. Chim.*, Series 3, vol. xxi.-xxii., No. 2.

* We have tried to effect this desiccation at a low temperature, and we thus obtained the yellow-brown body.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

Second Paper.—The Determination of the Cobalt in Cobaltous Bromide.

By THEODORE WILLIAM RICHARDS and GREGORY PAUL BAXTER.

(Concluded from p. 209).

Since it would be impossible to calculate the weight of the soluble bromides from the weight of the silver bromide without a quantitative analysis of the two bases present, the effort was made to evaporate the aqueous extract from the reduced cobalt, and to weigh the dried residue directly. In the work upon nickel, this method was necessarily rejected because the spongy nickel was oxidised and went into solution as nickelous hydrate, which could not be removed by filtration. Our spongy cobalt oxidised much more rapidly than the nickel upon treatment with water; but the decantate, upon filtration and evaporation in the air, deposited most of its cobalt as cobaltic hydroxide. The presence of salts of the alkalis greatly increases this oxidation, cobalt which has once been leached being oxidised but little. Heat also increases the oxidation, and so probably does the galvanic action with the platinum dishes which were used wherever possible through the whole course of this investigation.

In view of the colloidal solubility of nickelous hydrate in water, it is probable that cobaltous hydrate possesses the same property. When cobalt is treated with water in the presence of air, the metal oxidises and goes into solution as *cobaltous* hydrate; this is then further oxidised by exposure of the solution to the air and thrown out of solution as *cobaltic* hydrate, which can be filtered off. Since the dissolved cobalt is almost completely removed by this process, it is obviously legitimate to weigh the residue obtained by evaporating the aqueous extract of the reduced cobalt, and thus to obtain directly the amount of impurity present in the metal. This difference of procedure in the two cases is an interesting example of the way in which subordinate side reactions may influence two researches otherwise unusually analogous.

In the next four analyses (5 to 8) the cobalt was leached with the purest hot water in a platinum dish, and the solution, after filtration, was evaporated to dryness. The residue was taken up with water, filtered from the deposited cobaltic hydroxide into a weighed platinum crucible, again evaporated, heated to 130°, and weighed.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiv., No 14, February, 1899.

That these residues contained cobalt was undoubtedly true, from the fact that they were coloured a pale blue both after evaporation and after heating. During the heating, however, a slight blackening took place, which was due to the oxidation of traces of unoxidised cobaltous hydrate. In order to make sure that all unreduced bromides had been removed from the cobalt by the process of leaching, in each analysis the metal was dissolved by cold very weak nitric acid* and treated with silver nitrate. As not even the faintest cloudiness was ever again visible in these solutions, it was assumed that the soluble matter had been completely removed.

In Analysis 5 the bromine in the residue was determined and the result found to be considerably too low to correspond with the weight of the residue, if calculated as sodium bromide. In order to discover the cause of this discrepancy, an elaborate series of experiments was carried out at the expense of much time and labour. To describe these experiments in full would result only in confusing the mind of the reader. It is sufficient to say that pure spongy cobalt was treated with varying amounts of pure sodium bromide in solution, the conditions being regulated so as to be as nearly as possible like those in the analyses. The following conclusions drawn from these experiments are of great importance.

In the first place, no bromine is lost by the residues either during evaporation or in heating to 130°. The cobalt in the residues may be present in three forms: as cobaltous hydrate which has escaped oxidation, as cobaltic hydrate, and as unreduced cobaltous bromide,† each in exceedingly small amounts. The doubt as to the quantity of each present makes it impossible to apply the correction for dissolved cobalt with any degree of accuracy, and in the table of results no attempt has been made to do so. In the later analyses this cause of uncertainty was removed. This correction within a correction is, however, an infinitesimal of the second order; neglecting it can produce no serious effect upon the accuracy of the final result.‡ In this respect the research upon cobalt differs from that upon nickel, where the amount of hydroxide in the residue was relatively great, owing to the fact that it had not been chiefly eliminated by oxidation during the evaporation.

The possibility of the presence of some other acid than hydrobromic acid in the residues led us to make tests in this direction. Silicic acid was of course the first one to suggest itself. Early in the work one test had been made by subliming about 2 grms. of pure cobaltous bromide from a platinum boat in a current of hydrobromic acid gas. After the sublimation of the bromide the boat was perfectly bright, and gave not the slightest evidence of the presence of any silica. One of the residues was now treated with pure strong hydrochloric acid, heated to 130°, again treated with hydrochloric acid, and filtered. The amount of silica found, 3 one-hundredths of a m.grm., is a negligible quantity. Although the purity of the phosphoric anhydride used for drying our gases had been proven by passing air through a tube filled with the pentoxide into aqua regia, which upon evaporation gave no precipitate with ammonic molybdate, nevertheless one of the soluble residues from the reduced cobalt was tested with the same reagent with a negative result.

Upon examining one of the earlier residues for sulphuric acid, however, a slight precipitate of baric sulphate was formed. The source of this sulphuric acid was hard to discover, but finally it was found that the strong sulphuric acid in some of the drying columns had become discoloured in places by organic matter. This must have led to a slight decomposition of the acid and formation of sulphur dioxide, which was subsequently oxidised to sulphuric acid by the bromine. The amount of sulphuric acid present in the bromide was very small, 3·88 grms. of cobaltous bromide giving only 0·00036 grm. of baric sulphate in one case. As in the instance of nickel, however, this cause of error was wholly eliminated in the later experiments, and no trace of sulphuric acid could be detected in the material used in the last series.

The conclusions to be drawn from these experiments seem to be:—

First.—That our cobaltous bromide was almost if not completely reduced.

Secondly.—That the impurities, which consist of alkaline bromides (with, in some cases, a minute trace of sulphates), can be completely removed by leaching the cobalt.

Thirdly.—That the residue obtained by evaporating the water extract of the cobalt after reduction represents, within an exceedingly small amount, the weight of the impurities.

In the fourth series, during which the truth of this third conclusion was not realised, and a method similar to that used in the nickel research was adopted, the weight of the residue had to be calculated. The basis of calculation was the knowledge obtained from Analysis 5, Series V. Unfortunately this is the only analysis of material similar to that used in Series IV., where both the weight of the residue and the silver bromide obtained from it were determined. Since, however, the use of this analysis causes the average of Series IV. to approach within one part in thirty thousand of the average of Series V. and VI., we may safely assume that the rather meagre data represent with great exactness the real weight of the impurity contained in this Sample I. of cobaltous bromide. In Series V. and VI. the residues were weighed directly, so that this factor was not needed. Below are given the results of the first two series of analyses.

The Atomic Weight of Cobalt.

O = 16. Br = 79·955.

FOURTH SERIES (PRELIMINARY).—$CoBr_2$: Co.

No. of analysis.	Sample of $CoBr_2$.	Observed weight of cobaltous bromide in vacuum.	Observed weight of cobalt in vacuum.	Weight of AgBr found from residue.	Weight of residue calculated from AgBr.	Atomic weight of cobalt.
		Grms.	Grms.	Grm.	Grm.	
1.	I.	5·59216	1·50873	0·00309	0·00193	59·007
2.	I.	4·61944	1·24807	0·00681	0·00426	58·996
3.	I.	3·75291	1·01713	0·01267	0·00793	58·989
4.	I.	3·00645	0·81409	0·00815	0·00510	59·007
					Average	59·000

FIFTH SERIES.—$CoBr_2$: Co.

No. of analysis.	Sample of $CoBr_2$.	Observed weight of cobaltous bromide in vacuum.	Observed weight of cobalt in vacuum.	Weight of residue.	Corrected weight of cobaltous bromide.	Corrected weight of cobalt.	Atomic weight of cobalt.
		Grms.	Grms.	Grm.	Grms.	Grms.	
5.	I.	5·32955	1·44189	0·00761*	5·32194	1·43428	58·996
6.	I.	7·51430	2·02965	0·00644	7·50786	2·02321	58·989
7.	II	2·32910	0·62957	0·00280	2·32630	0·62677	58·973
8.	II.	7·45336	2·01378	0·00642	7·44694	2·00736	59·011
					Average		58·992

* From the residue in Series V., Analysis 5, was obtained 0·01216 grm. of argentic bromide. Hence 0·0010 grm. of argentic bromide corresponds to 0·000626 grm. of residue. This factor is used in calculating the results in Series I.

* In a platinum dish this solution takes place with great ease, and with no danger of a loss of bromine. The galvanic action is a great assistance.

† Cobaltous bromide could only have found its way into this residue by having been protected from reduction by enclosure in crystals of sodic bromide. It must have been exceedingly small in amount, if present at all.

‡ This extra cobalt may partly explain why the sum of the total analysis slightly exceeds 100·000 per cent.

It seemed highly important to us at this point to prepare cobaltous bromide which should be free from every impurity. In the first place the drying apparatus was slightly modified, no strong sulphuric acid being used except in drying the air necessary for sweeping the nitrogen out of the weighing bottle. Dilute sulphuric acid was substituted in every case, and two columns of stick potash followed by one of phosphoric anhydride were inserted beyond this dilute acid. As the porcelain tubes had evidently been the source of the alkaline impurities found, a platinum lining, made by bending a large piece of platinum foil into the form of a cylinder, was provided for the outside porcelain tube (compare with the paper on Nickel, *Proc. Amer. Acad.*, xxxiv., p. 331). The smaller porcelain tube was not used at all, the sublimed material being removed by taking out the foil and unfolding it. Cobalt from Sample III. was then sublimed in the remodelled apparatus from a platinum boat. The material obtained in this way gave results for the atomic weight altogether too high—a circumstance due to large quantities of platinum actually found in the sublimed bromide. Even here a small amount of alkaline impurity existed, having crept in through the crack in the platinum foil. Hence, no more work was done with this material; but renewed precautions were taken to prepare by the older method cobaltous bromide which should contain the smallest possible number and quantity of impurities.

Four analyses were made with this new material, which proved in spite of all our care to contain as much soluble matter as before. The water extracts from these analyses were evaporated in a flat platinum dish, which exposed a large surface of the solution to the air. This served to oxidise completely the dissolved cobaltous hydrate, for the residues did not become grey when heated, and upon the addition of water gave perfectly clear solutions. These residues were faintly blue, the colour being due doubtless to a trace of unreduced cobaltous bromide. For some undiscovered reason, the amount of silver bromide obtained from the residues was still too small to correspond to the weight of the residue if calculated as sodic bromide.

Tests were repeated for sulphuric, phosphoric, and silicic acids with the greatest possible care, but still with negative results. In one analysis the cobalt was determined in the residue and found to be only 0·00013 grm. It is possible, however, that these few tenths of a m.grm. discrepancy are due to the presence of all or at least several of the above-mentioned acids combined with sodium, each in quantity too minute for detection; and for the present this will have to rest as the explanation.

Weight of residue.	Weight of AgBr obtained from residue.	NaBr in residue, calculated from AgBr.	Unidentified.
0·00306	0·00439	0·00240	0·00066
0·00643	0·00978	0·00536	0·00107

Sixth Series.—$CoBr_2$: Co.

No. of analysis.	Sample of $CoBr_2$.	Observed weight of cobaltous bromide in vacuum.	Observed weight of cobalt in vacuum.	Weight of residue.	Corrected weight of cobaltous bromide.	Corrected weight of cobalt.	Atomic weight of cobalt.
		Grms.	Grms	Grm.	Grms.	Grms.	
9.	III.	5·11197	1·38027	0·00306	5·10891	1·37721	59·016
10.	III.	6·41822	1·73333	0·00483	6·41339	1·72850	58·999
11.	III	6·60707	1·78778	0·00902	6·59805	1·77876	59·021
12.	III.	3·03497	0·82249	0·00643	3·02854	0·81606	58·982

Average .. .. 59·004

Average of Series V. and VI. .. .. Co = 58·998

This final average differs from that published before by only about one part in ten thousand; but in comparing the two, one must remember that the material used last year must have been contaminated by the same impurities which have been discussed in this paper. If the impurity contained as much bromine as cobaltous bromide contains, it would have had no effect upon last year's results. In the case of *nickel*, where the impurity consisted wholly of sodic bromide, the effect of correcting the observed results in the paper of 1897 was to raise the atomic weight of nickel from 58·688 to 58·703. The impurity from our *cobaltous* bromide, on the other hand, contained unknown substances in quantities so small as to elude detection, but large enough to change the sign of the corresponding correction. Thus 22·63 grms. of cobaltous bromide in Series V. (the series in which the materials most nearly resembled those used in Series II. and III. of last year's work) were found to contain 0·02327 grm. of impurity. If, as we may reasonably suppose, all the residues obtained from this sample of material resembled that found in Analysis V., Series V., this residue would have yielded 0·0372 grm. of argentic bromide. We may now correct last year's results by subtracting from the several weights of cobaltous bromide proportional weights of impurity, and also subtracting from the several weights of argentic bromide amounts of this substance corresponding to the impurity. Making this correction, the atomic weight of cobalt would be *lowered* 0·008, the averages of Series II. and III. becoming 58·987 and 58·979. Our uncertainty regarding the nature and amount of the impurity thus involves an uncertainty of about one part in six thousand in last year's results. In the light of all the circumstances, it is perhaps safest not to attempt any correction of these values, but to accept them uncorrected as subject to this possible error. The results are accordingly given below in an uncorrected form.

The data just discussed obviously afford a basis for recording the total percentage composition of the cobaltous bromide analysed.

Complete Analysis of Cobaltous Bromide.

(Based upon Series II., III., and V.).

			Per cent.
Cobalt (Series V.)			= 26·923
Total bromine	(II.) 73·050 % (III.) 73·053 % Aver. 73·051 %	= Bromine combined with cobalt	= 72·981
		Bromine actually found in impurity.	= 0·070
Total impurity .. = 0·103 %		= Remainder of impurity (chiefly sodium)	= 0·033
Total			= 100·007

Series VI., perhaps the best of all, is not included in this table, because the material used in it was not quite identical with that used in the three other series. Obviously it is possible to calculate two more ratios involving the atomic weight of cobalt, in which the values for the *bromine* in the bromide are compared with the cobalt found in it. Into this calculation the weight of the bromide itself enters simply as a constant, and an indifferent impurity (such as water) would be eliminated from the result. The table below includes all of the five possible ratios obtainable from our work, Series I. and IV. being rejected because they were merely preliminary:—

$2AgBr : CoBr_2$	(Series II.)	58·995
$2Ag : CoBr_2$	(Series III.)	58·987
$CoBr_2 : Co$	(Series V. and VI.) ..	58·998
$2AgBr : Co$	(Series II. and V.)	58·994
$2Ag : Co$	(Series III. and V.) ..	58·992
	Average	58·993

This table, although giving an interesting statement of the possible combinations, does not yield a fair average—for Series V. is introduced three times, Series II. and III. each twice, while Series VI., which is at least as accurate as the others, appears only once. A fairer method would probably be to avoid all hypotheses and combinations, and assign to each of the four series equal weights, as follows:—

Series II. (uncorrected)	.. ..	Co = 58·995
Series III. (uncorrected)	.. ..	Co = 58·987
Series V. (corrected)	.. .. ..	Co = 58·992
Series VI (corrected)	.. .. ..	Co = 59·004
	Final average	58·995

Obviously it makes but little difference which method we adopt; the averages are essentially identical. The highest individual experimental result among all these determinations was 59·021 and the lowest 58·995, the average variation from the mean 58·995 being 0·012. Because these results are less concordant than one could wish, and the conclusion is somewhat less positive than that reached in the case of nickel, the atomic weight of cobalt is being further studied by radically different methods in this Laboratory.

In a recent article (*Zeit. Anorg. Chem.*, xvii., 236), Professor Winkler calls attention to some possible errors in the work upon both nickel and cobalt published last year. That the disagreement between his results and ours is due to the methods employed by him in his work upon these two elements has been sufficiently shown in the preceding paper upon the atomic weight of nickel. In addition, however, his several suggestions concerning our own work should obviously be reviewed and discussed in detail.

His specific criticisms are four in number. First, he suggests that the porcelain tubes might have been attacked during the sublimation of the bromides, with the introduction of foreign bromides into the nickelous and cobaltous bromides. He goes on to state that the bromides were dried in an acid atmosphere, and probably retained hydrobromic acid after this gas had been displaced by air. His third criticism is that the nickelous bromide in the earlier analyses contained nickelous oxide which had to be determined and subtracted; and his final objection applies to the use of the Gooch crucible.

Answers to the greater part of his criticisms can be found in the very articles which he criticises. In one case only can his view be substantiated—the porcelain tubes are really attacked. That this flaw was a possibility we realised at the time; but we also realised the smalless of the error introduced by even a comparatively large amount of such impurity. This matter has been already discussed in detail, both in this paper and in the paper upon the atomic weight of nickel.

There are two possible ways in which hydrobromic acid could have been retained—by absorption and by inclusion. At the high temperatures employed the absorption must have been very slight, and the long process of washing with an indifferent gas was favourable to the elimination of any tendency in that direction. While the inclusion of *liquids* is a very serious possible cause of error, that of *gases* is usually negligible because of the small mass involved. For this reason crystallisation from solutions is far less satisfactory than sublimation as a means of purification.

That as a matter of fact our bromides were neutral there is no lack of evidence. The possibility of acidity had occurred to us also, but reasoning from analogy we had decided that this possibility was rather an improbability. Bromides and chlorides of barium and strontium, heated in the same way in a dry acid atmosphere, after the acid has been displaced by dry air, give absolutely neutral reactions with methyl orange (*Proc. Amer. Acad.*, xxix., 59; xxx., 373). With cobaltous bromide the end point is not as easy to detect as with the before-mentioned halides, on account of the colour of the dissolved salt, but colorimetric comparison makes it possible to distinguish the change very accurately. A solution of our cobaltous bromide containing methyl orange perceptibly changed colour upon the addition of the minimum amount of hundredth normal acid necessary to produce a change of colour in pure water containing methyl orange, showing that the salt must have been very near if not at the turning-point. As a final test, potassium bromide was sublimed in the apparatus which had been used for the preparation of the cobaltous bromide. The sublimate was then heated in a current of dry nitrogen and hydrobromic acid gas, and finally, when cool, the nitrogen and acid were displaced by dry air, just as in preparing the cobaltous bromide for analysis. This potassic bromide upon solution gave an absolutely neutral reaction with methyl orange. Taking into consideration these three points, one cannot believe that enough hydrobromic acid was retained to have had an appreciable influence on our results.

The third critcism, objecting to the fact that in some analyses a small amount of nickelous oxide was found in the bromide, is an unfortunate one. A careful perusal of the work would have shown that only in the preliminary series of results was this the case, and that this series does not enter into the final average, although its results differ only by a very small amount from those subsequently obtained with material free from oxide. As far as the nickel is concerned, a conclusive proof of the absence of acid is afforded by this very fact that the earlier determinations, in which it was necessary to filter off a residue of finely divided nickelous oxide, gave results no higher for nickel than the later results.* Hence the second and the third criticisms are obviously inconsistent with one another.

The advantages of the Gooch crucible are too well known to need mention. Professor Winkler's specific objection to the collecting of displaced asbestos upon an ordinary filter affects only an amount of a few tenths of a m.grm.; and a proof that no error was introduced in this way lies in the fact that in every case the amount of silver bromide found agreed very closely with the amount of silver necessary to complete the reaction, where all but a few tenths of a per cent of the silver was weighed out, and the remainder was added volumetrically. The following brief table will make this clear.

Thus, in the cobalt work, 18·16302 grms. of silver yielded 31·61642 grms. of silver bromide,—a ratio of 57·448 to 100·000,—while in the case of nickel, 15·51556 grms. of bromide gave 26·67078 grms. of silver bromide,—a ratio of 57·444 to 100·000, while Stas found 57·445.

From the cobalt work	AgBr : Ag = 100·000 : 57·448
From the nickel work	AgBr : Ag = 100·000 : 57·444
From Stas's work ..	AgBr : Ag = 100·000 : 57·445

Thus the last of Professor Winkler's criticisms is sufficiently answered.

After necessarily dwelling at such length upon disagreements, it is a pleasure to emphasise other points in which we agree with Professor Winkler. The evidence of our work, together with Dr. Cushman's, strongly supports Winkler's contention that nickel and cobalt, as we know them of old, cannot contain more than an infinitesimal amount of any unknown element. Several radically different methods of preparation and many fractionations invariably led us to constant atomic weights, within a reasonable limit of experimental error; and we are forced to conclude that the familiar properties of these common and useful metals are to be ascribed to elements as definite as any of the seventy-five. It is needless to point out also that we agree with Professor Winkler in assigning to cobalt a higher atomic weight than to nickel, in spite of

* The slight colloidal solubility of nickelous hydroxide was evidently destroyed by the presence of large amounts of nickelous bromide, as one would expect.

the conflict of periodicity with rhodium and palladium. According to our results, the atom of cobalt, weighing almost exactly 59·00, is very nearly half of 1 per cent heavier than that of nickel.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 20th, 1899.

Professor Thorpe, F.R.S., President, in the Chair.

(Concluded from p. 212).

55. "*β-Isopropylglutaric Acid.*" By F. H. Howles and Jocelyn F. Thorpe.

β-Isopropylglutaric acid was originally prepared by Schryver, by the reduction of terpenylic acid and synthesised by him in small quantities by the action of ethylic sodiomalonate on ethylic isobutylenemalonate (*Trans.*, 1893, 1345); later, Knoevenagel (*Ber.*, 1898, xxxi., 2585) prepared it by the condensation of isobutaldehyde with ethylic malonate; Schryver's acid melted at 99—100°, Knoevenagel's at 96·5—97°. The authors find that by far the largest yield of this acid is obtained in the following way.

Ethylic β-isopropylacrylate, $Pr\beta.CH{:}CH{\cdot}CO_2Et$, prepared by eliminating hydrogen bromide from ethylic α-bromisobutylacetate by means of diethylaniline, is a mobile liquid boiling at 174°, which, on condensation with ethylic sodiocyanacetate in alcoholic solution, gives a mixture of a neutral and a hydrogen ethylic salt. Ethylic α-cyano-β-isopropylglutarate, $EtO_2C{\cdot}C(CN)H{\cdot}CH(Pr\beta){\cdot}CH_2{\cdot}CO_2Et$, is a colourless oil boiling at 195° (30 m.m.), whilst the hydrogen ethylic salt, $HO_2C{\cdot}C(CN)H{\cdot}CH(Pr\beta){\cdot}CH_2{\cdot}CO_2Et$, is a dark coloured oil which splits off carbon dioxide on distillation and passes into ethylic γ-cyano-β-isopropylbutyrate, $CN{\cdot}CH_2{\cdot}CH(Pr\beta){\cdot}CH_2{\cdot}CO_2Et$, a mobile liquid boiling at 234°.

The neutral ethylic salt on hydrolysis with methyl alcoholic potash, yields a solid potassium salt, which, on boiling a short time with concentrated hydrochloric acid, becomes the imide,—

$$(Pr\beta)CH\!<\!\begin{matrix}CH_2CO\\CH_2CO\end{matrix}\!>\!NH,$$

a solid substance crystallising from water in lustrous plates melting at 120°, and which is quantitatively converted into β-isopropylglutaric acid on boiling for two hours with a 50 per cent solution of sulphuric acid.

β-Isopropylglutaric acid,—

$$HO_2C{\cdot}CH_2{\cdot}CH(Pr\beta){\cdot}CH_2{\cdot}CO_2H,$$

prepared either in this way or by the direct hydrolysis of the hydrogen ethylic salt with sulphuric acid, crystallises from water in needles melting at 100°, and on treatment with acetyl chloride yields a liquid anhydride boiling at 171° (30 m.m.), and an anilic acid crystallising from dilute alcohol in plates melting at 121°.

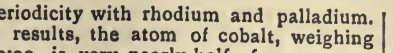
This acid does not appear to be identical with that obtained by Angeli and Rimini (*Gazz. Chim.*, xxvi., 36) from isocamphor on oxidation with potassium permanganate, which melts at 96° and gives an anhydride melting at 60°; further, the dissociation constant K 0·0646 of the authors' acid, as found by Mr. Lidbury, does not agree with K 0·0052 of Angeli and Rimini's acid.

56. "*The Synthesis and Preparation of Terebic and Terpenylic Acids.*" By W. Trevor Lawrence.

The tertiary hydrogen atom in monobasic aliphatic acids is readily oxidised by potassium permanganate (R. Meyer and Fittig).

The author has applied this method to the synthesis of terebic and terpenylic acids.

β-Isopropylglutaric acid is readily oxidised by chromic acid mixture, with the formation of terpenylic acid, confirming Wallach's formula for this acid, namely,—



The synthetic acid is identical with the acid obtained by oxidation of oil of turpentine, melting when anhydrous at 89°, and with 1 mol. H_2O at 56°. It is oxidised by permanganate with formation of terebic acid, and gives the characteristic silver salt, $C_8H_{11}O_4Ag$.

Isopropylsuccinic acid is also easily oxidised by chromic acid mixture to terebic acid, $C_7H_{10}O_4$, which is identical in all respects with the acid obtained by the oxidation of oil of turpentine.

The synthetic acid melts at 175°, and gives the characteristic barium salt of diaterebic acid, $C_7H_{10}O_5Ba,3H_2O$. Under similar conditions, ββ-dimethylglutaric acid remains unchanged.

The yield of the lactone acid is 50 to 60 per cent, the rest being unchanged acid.

Further, it is shown that the separation of terebic and terpenylic acids is easily and completely effected by spreading the mixture of acids on porous plates and heating at 90°; the terebic acid remains as a dry powder on the surface of the plate, and the terpenylic acid is obtained by extracting the plate with water. The author is further engaged in investigating the oxidation products of other similarly constituted acids, and also the action of hydrobromic acid on terebic and terpenylic acids.

57. "*Position-isomerism and Optical Activity: the Comparative Rotatory Powers of Methylic and Ethylic Ditoluylglycerates.*" By Percy Frankland, F.R.S., and Henry Aston.

This forms a continuation of the work on the same subject by P. Frankland, McCrae, and Wharton (*Trans.*, 1896, lxix., 1309, 1583; 1898, lxxiii., 307; 1899, lxxv., 337), the authors having prepared and examined the methylic and ethylic salts of the three isomeric ditoluylglyceric acids. Methylic di-*p*-toluylglycerate (inactive) melts at 98°, the corresponding active salt at 102°; ethylic di-*p*-toluylglycerate melts at 69°; all the other compounds are liquids. The following are the specific rotations:—

Methylic di-*p*-toluylglycerate	..	$[\alpha]_D^{20°}$	$=+41{\cdot}21°$
Ethylic ,,	..	,,	$=+42{\cdot}41$
Methylic di-*m*-toluylglycerate	..	,,	$=+26{\cdot}40$
Ethylic ,,	..	,,	$=+26{\cdot}89$
Methylic di-*o*-toluylglycerate	..	,,	$=+20{\cdot}19$
Ethylic ,,	..	,,	$=+21{\cdot}64$

The corresponding dibenzoylglycerates, previously prepared by P. Frankland and MacGregor (*Trans.*, 1896, xix., 104) have the following rotations:—

Methylic dibenzoylglycerate	(m.p. 58·9°)	$[\alpha]_D^{20°}$	$=+26{\cdot}67°$
Ethylic ,,	(m.p. 25°)	,,	$=+26{\cdot}08$

Thus in this series, again, the *p*-toluyl group has the greatest, and the *o*-toluyl group the least, rotatory effect. The rotatory effect of the benzoyl is almost identical with that of the *m*-toluyl group.

The dextrorotation of all these compounds diminishes with increase of temperature.

The rotatory effects of the isomeric toluyl groups is again found to follow in the same order as that of their molecular volumes, the *p*-toluyl having the largest, and the *o*-toluyl-compounds the smallest, molecular volumes. The molecular volumes of all these compounds are distinctly in excess of the values calculated by means of Traube's formula, and thus afford no evidence of association.

58. "*Fencholenic Acid.*" By G. B. Cockburn, B.A., B.Sc.

The author shows that fenchonoxime, by treatment

with dilute sulphuric acid, gives, not one nitrile, as Wallach states (*Annalen*, 1891, cclxiii, 136), but a mixture of two isomerides. Of these, one (β) passes easily on saponification to a solid unsaturated acid, $C_9H_{15}CO_2H$, m. p. 72—73°, b. p. 259—260°. The other (α) is very stable, and only gives an acid after long saponification. This acid is isomeric with the former, but is liquid, and boils at 254—256°. Wallach describes the acid he obtained as a liquid, but it is probably a mixture of the above α- and β-acids. The boiling-point of the nitrile, as given by Wallach, is 217—218°, whilst that of the pure β-nitrile re-formed from the pure acid is 211—212°, and of the α- 217—219°. Owing to the difference in behaviour of these two nitriles towards alcoholic potash, the separation of the two acids is comparatively simple.

This behaviour of fenchonoxime bears out the analogy existing between camphor and fenchone. The oximes of both these bodies, by the action of dilute acid, lose a molecule of water in two different ways, and give two isomeric unsaturated nitriles in each case; and these in their turn yield two corresponding acids, one solid, the other liquid.

59. "*The Action of certain Acidic Oxides upon Salts of Hydroxy-acids.*" Part IV. By G. G. HENDERSON, D.Sc., M.A., T. W. ORR, and R. J. G. WHITEHEAD.

The paper contains the results of investigations carried on in continuation of those formerly communicated to the Society (*Trans.*, 1895, lxvii., 102 and 1030; 1896, lxix., 1451), and a discussion of the constitution of the compounds of the tartar emetic type.

Sodium, *potassium*, and *ammonium molybdicitrates* were prepared by boiling molybdenum trioxide with aqueous solutions of the corresponding primary citrates. They have the formulæ $MoO_2(C_6H_6O_7M')_2,xH_2O$, crystallise in colourless prisms, are readily soluble in water, and are decomposed by heat or light. The barium salt, $MoO_2(C_6H_6O_7)_2Ba,5H_2O$, obtained by precipitation, is a white crystalline powder almost insoluble in water. Decomposed by dilute sulphuric acid it yields a solution which appears to contain molybdicitric acid, $MoO_2(C_6H_7O_7)_2$.

Tungstic oxide, boiled with solutions of mono-alkali citrates, gave *double tungsticitrates* of the formula $WO_2(C_6H_6O_7M')_2,C_6H_7O_7M',xH_2O$; the simple salts are not obtained. These salts form small, colourless crystals, very readily soluble in water, and are not decomposed when heated to 120°. The double barium salt, $2WO_2(C_6H_6O_7)_2Ba$, $(C_6H_7O_7)_2Ba,10H_2O$, prepared by double decomposition, crystallises in minute needles, soluble in water.

Sodium, *potassium*, and *ammonium molybdimalates*, $MoO_2(C_4H_4O_5M')_2,xH_2O$, were prepared like the molybdicitrates. The potassium salt crystallises in large, the sodium salt in small, colourless prisms, and the ammonium salt is a white crystalline powder. All are readily soluble in water, and easily decomposed by exposure to heat or light. Another molybdimalate of sodium, of the formula $MoO_2:C_4H_3O_5Na,1\frac{1}{2}H_2O$, was prepared by heating a solution of monosodium malate with excess of molybdic oxide. It crystallises in long colourless needles, which are soluble in water, is very sensitive to light, and is decomposed by heating to about 90°.

Tungstic oxide is only dissolved with difficulty by solutions of alkali malates, but some *tungstimalates*, $WO_2(C_4H_4O_5M')_2,xH_2O$, were prepared. The sodium salt crystallises in small, the potassium salt in long, needles, the ammonium salt in delicate leaflets. They are readily soluble in water, and can be heated to 105° without decomposition.

With solutions of mono-alkali mucates, molybdic oxide gives in the first instance unstable double salts, $2(MoO_2{\cdot}C_6H_7O_8M')$, $C_6H_9O_8M',xH_2O$, which are easily soluble in water, and yield the simple *molybdimucates*, $MoO_2:C_6H_7O_8M',xH_2O$. The potassium and ammonium salts are white crystalline powders, fairly easily soluble in water, and decomposed by heating to about 90°. When dry they are fairly stable to light, but their solutions are quickly acted upon.

Potassium tungstimucate, $WO_2:C_6H_7O_8K,3H_2O$, was prepared similarly, but with difficulty. It forms minute lustrous crystals, and is extremely readily soluble in water, and more stable towards heat or light than the molybdimucate.

Potassium molybdilactate, $MoO_2(C_3H_4O_3K)_2$, the only crystalline derivative of lactic acid we have succeeded in preparing, was obtained in the form of small colourless crystals, very readily soluble both in water and in dilute alcohol. It is not very sensitive to light when dry.

Silica was found to be almost insoluble, even when used in the hydrated state, in solutions of all the salts examined.

Sodium, *potassium*, *ammonium titanitartrates*, $TiO(C_4H_4O_6M')_2,xH_2O$, were prepared in the usual way. Hydrated titanic oxide was used, because the anhydrous oxide is practically insoluble in solutions of tartrates. The salts crystallise in small colourless prisms readily soluble in water. Alcohol precipitates from a solution of the ammonium salt a crystalline solid whose composition approximates to the formula $TiO:C_4H_3O_6NH_4$. A white barium salt, almost insoluble in water, is obtained by precipitation.

The corresponding *stannitartrates*,—

$$SnO(C_4H_4O_6M')_2,xH_2O,$$

were prepared similarly. They form small colourless crystals, fairly easily soluble in water. Heating of their solutions in water for any length of time causes slow decomposition of the salts, but in the dry state they are quite stable. From solutions of the potassium and ammonium salts, alcohol precipitates crystalline solids, which appear to have the formula $SnO:C_4H_3O_6M'$. A white barium salt, almost insoluble in water, was also prepared.

Potassium titanicitrate, $TiO(C_6H_6O_7K_2),H_2O$, and *ammonium stannicitrate*, $SnO(C_6H_6O_7NH_4)_2,\frac{1}{2}H_2O$, were obtained by a similar process, though with some trouble. They form small white crystals, very readily soluble in water and soluble in dilute alcohol. They are stable when dry, but gradually decompose if their aqueous solutions are heated.

The hydrated dioxides of titanium and tin were found to dissolve in boiling aqueous solutions of mono-alkali malates, but no definite compounds were isolated.

With some difficulty a *potassium titanimucate*, $TiO:C_6H_7O_8K,3H_2O$, was prepared in the form of small white crystals, easily soluble in water, not sensitive to light, and not decomposed at 100°. No corresponding compound of tin could be obtained.

Collective Index.

Fellows can obtain the Collective Index 1873—1882 from the Assistant Secretary at the price of 10s., or 11s. including carriage. The price of the Collective Index 1883—1892 is 16s. including carriage.

Research Fund.

A meeting of the Research Fund Committee will be held in June. Forms of applications for Grants can now be obtained from the Assistant Secretary.

Silver Sub-oxide.—M. Guntz.—The author has succeeded in proving the existence of sub-oxide of silver, Ag_4O, and preparing the compound by the decomposition of silver oxide, Ag_2O, by heat. Ag_2O begins to decompose slowly at about 250°; at the end of a sufficiently long time the decomposition is complete. After many attempts, the tension of dissociation of Ag_4O was determined.—*Comptes Rendus*, cxxviii., No. 16.

NOTICES OF BOOKS.

Commercial Organic Analysis. By Alfred Allen, F.I.C., F.C.S. Third Edition. Illustrated. With Revisions and Addenda, by the Author and Henry Leffmann, M.A., M.D. Vol. ii., Part I. London: J. and A. Churchill. 1899. Pp. 387.

The matter dealt with in this volume is the analysis of fixed oils, fats, waxes, glycerol, nitroglycerin, and nitroglycerin explosives; but far the greater part of the book is taken up with oils and fats, their extraction, purification, physical and chemical properties, classification, examination, and identification: there are also given a number of special methods for the examination of fatty oils of all kinds.

The revision has been of a most extensive character, involving every page and almost every paragraph, but, in deference to the author's expressed disapproval of the spelling advised by the American Association for ths Advancement of Science, it has not been adopted in this (American) edition, and any instances which may occur are accidental; for this we are thankful.

Some of the most important additions to this volume are:—The bromine thermal method, methods for the determination of glycerol, acetyl number, various tests for the oxidation of oils, composition and official methods for the examination of dynamite and smokeless powders, dégras and cloth oils.

The volume is well and clearly printed, and furnished with a copious index.

Matriculation Directory, No. XXV. The University Tutorial Series. London: W. B. Clive. 1899.

The contents of this book consist principally of old examination papers, and the answers to the questions set. By reading through these the student will get an idea of what sort of questions he will probably have to tackle. This, with articles on the special subjects for June, 1899, and January, 1900, will help him to pass the examination. He will then be ready for more serious study.

Outlines of Industrial Chemistry; a Text-book for Students. By F. H. Thorp, Ph.D., Instructor in Industrial Chemistry in the Massachusetts Institute of Technology. New York: The Macmillan Co. London: Macmillan and Co., Ltd. 1898. Pp. 541.

The wide range of subjects covered by this interesting work prevents any particular process being dealt with exhaustively and completely; the object of the author has, in fact, been to give the outlines of the more important chemical industrial processes, leaving the matters of detail to be acquired by reference to the more comprehensive handbooks and special works.

The author has assuredly succeeded in his endeavour, and has given us a valuable work which cannot fail to be appreciated.

The book is divided into two parts: Part I., on Inorganic Industries, and Part II., on Organic Industries. The first part includes such industries as the manufacture of acids, salt, soda, alkalis, fertilisers, lime, glass, pigments, matches, &c., while Part II. deals with the destructive distillation of wood and bones, the manufacture of illuminating gas, including acetylene and air gas, coal-tar and its derivatives, animal, mineral, and vegetable oils, soaps, resins, starch, sugar, and fermentation industries. The latter covers the wide field of brewing, wine-making, and distilling, also the manufacture of vinegar. Explosives (mainly for industrial purposes) and the textile industries (including fibres, bleaching, mordants, dye-stuffs and dyeing, and textile printing) cover a good number of pages. Paper-making, leather and the tanning industries, and the manufacture of glue, complete the book, A large number of references to Standard Works, Encyclopædias, and Technical Journals are given throughout the text.

The book is well printed and bound, and is furnished with an Index of twelve pages.

The Chemistry of Coke: being the "Grundlagen der Koks-chemie" of O. Simmersbach. Translated and Enlarged by W. Carrick Anderson, M.A., B.Sc. Glasgow and Edinburgh: William Hodge and Co. 1899. Pp. 159.

As the author very truly remarks, it is doubtful whether any extensive manufacture has been less scientific than that of coke; and considering the importance of the subject this is really remarkable,—even the recovery of the by-products is only now beginning to be developed on a large scale.

The manufacture of coke from coal was known and practised in the early part of last century, but its chemical examination only dates back about forty years; certain points had been found by practical experience, but those were known only to a small number of actual workers.

The Introduction of the book deals with the History of the Chemistry of Coke, references being made to the work of Stein, Richters, Muck, Parry, Knublauch, Crace-Calvert, &c. The purpose of coking and the use of coke is described in Chapter I., after which we find the theoretical and practical methods and yields of coking considered, with their influence on the form and appearance of the coke.

Coke is generally regarded only as carbon contaminated with a certain amount of mineral matter; but this view is not correct, as coke may also contain hydrogen, oxygen, nitrogen, and sulphur. The proportions present and the influence of these ingredients is dealt with in the chapter on the chemical composition of coke.

Chapter VII., on the examination of coal and coke, has been added by the translator; it contains methods and details of working which the author has himself found useful in practice.

The book should certainly be found useful to those engaged in the manufacture of coke, and we hope, with the translator, that it will contribute towards placing the industry on a more scientific basis.

Preliminary Report of an Investigation of Rivers and Deep Ground Waters of Ohio, as Sources of Public Water Supply. By The State Board of Health. Cleveland: J. B. Savage Press. 1898. Pp. 259.

This volume contains a series of reports connected with the chemical and bacteriological examination of waters, with a view to deciding whether or no they are suitable for public use. The methods used for carrying out these examinations are to a great extent the same as those used in England, with the exception of those used in the bacteriological examination. We also note that the use of agar is recommended for this work, as the hot summer of Ohio causes the gelatin plate cultures to melt. The reports are very complete, but are naturally only of local interest.

Solubility in Water of Substituted Malonic Acids.—G. Massol and F. Lamouroux.—The solubility of the first five terms of the series of mono-substituted malonic acids have been determined for temperatures between 0° and 50°. The results show that all these acids are very soluble in water, and if their solubilities are represented graphically as functions of the temperature, the curves are straight lines. The introduction of a hydrocarbon radical diminishes the solubility of malonic acid.—*Comptes Rendus*, cxxviii., No. 16.

CORRESPONDENCE.

SEPARATING TIN OXIDE FROM GANGUE.

To the Editor of the Chemical News.

Sir,—I beg to communicate for your esteemed consideration a method recently employed by me in reference to the separation of tin oxide (present in small quantities) from a siliceous gangue (present in relatively large quantities). As you are well aware such a problem has for years past proved a matter of great difficulty in the satisfactory assay of tin. My method is, briefly, to use Sonstadt's solution, by means of which the felspar and silica may be got rid of at once. With matter in a fine state of division I found vanning unsatisfactory in a high degree as contrasted with this method. The samples I first dealt with contained from six-tenths to two-tenths of a per cent of tin oxide, the gangue mostly siliceous and with a deal of felspar.—I am, &c.,

O. F. Colvin,
Consulting Mining Engineer,
Metallurgist, and Assayer,

21, York St., Moonee Ponds,
Melbourne, Australia,
March 28, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 16, April 17, 1899.

Heat of Formation and Combustion of some Nitrogen and other Compounds.—M. Berthelot and G. André.—The publication of M. Berthelot's paper on animal heat, suggested the determination of the rate of formation and of combustion of a number of substances found in the animal body and allied nitrogen compounds, which are interesting from a chemical or physiological point of view. Numbers were found for the following substances:—Cholesterine, glycollic and lactic nitriles, xanthine, paraphenylenediamine, nicotine, pyrrol, carbazol; and the indol series—indol, scatol, α-methyl indol, and oxindol. Each of these products was purified with great care and analysed, then the heat of combustion was determined at constant volume.

Solubility in Water of the Normal Acids of the Oxalic Series.—F. Lamouroux.—The author has examined the solubility in water of ten acids of the oxalic series at temperatures between 0° and 65°. The experiments were not continued above this temperature on account of decomposition taking place. The results show that acids with an even number of carbon atoms are relatively less soluble than those with an odd number, and that the solubility decreases rapidly with increased molecular weight. The two first acids, having an odd number of carbon atoms, are very soluble, but those that follow are not more soluble than their homologues of the even groups. Glutaric acid behaves in a peculiar manner; its solubility increases more rapidly than that of malonic acid.

Action of Ethylic, Isobutylic, and Isoamylic Alcohols on their Sodium Derivatives.—M. Guerbet.—Isoamylic alcohol, when heated to 150—160° with its sodium derivative, is partially transformed into diamylic alcohol, $C_{10}H_{22}O$, and isovaleric acid. Isobutylic alcohol scarcely reacts at all on its sodium derivative, even at a temperature of 210—215°; whilst ethylic alcohol, under the same conditions, is partially transformed into ethylene and sodic acetate,—

$$C_2H_6O+C_2H_5NaO=C_2H_4+C_2H_3NaO_2+2H_2.$$

The author proposes to continue this research on alcohols richer in carbon than amylic alcohol.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxi.-xxii., No. 1.

Absorption of Small Quantities of Carbonic Acid contained in Large Volumes of Gas.—MM. Marboutin, Pecaul, and Bouyssy.—The authors have succeeded in completely absorbing the carbonic acid contained in the air in the Montsouris Park by means of the following arrangement:—The air was made to circulate through an almost horizontal tube, 0·8 metre in length and 11 m.m. in diameter, containing 50 c.c. of a solution of potassic hydrate at 20 grms. per litre; the bubbles of gas joined together and pass through with a speed of about 4 litres per hour, being in contact with the absorbing liquid for at least fifteen to twenty seconds. A second identical tube, placed in continuation of the first, never showed the least trace of carbonation, either with potash or baryta, even after the passage of 200 litres of air. The alkalinity of the second tube was identical with that of the solution used.

Action of Benzoic and Formic Aldehydes on the Ammoniacal Salts.—M. Delépine.—The aromatic aldehydes are capable of giving two orders of isomeric compounds in uniting with ammonia. The first, or hydramides, are decomposed by acids into aldehydes and ammonia; the second are bases belonging to the group of glyoxalidines, not decomposed by acids. The author has shown, after studying the salts of furfurine, that this last property is in perfect accord with the calorimetric results he previously obtained. Thus the equation,—

$$C_{15}H_{12}N_2O_3,HCl \text{ sol.}+HCl \text{ in } 3H_2O = 3C_5H_4O \text{ liq.}+2NH_4Cl \text{ sol.},$$

which expresses the possible action of hydrochloric acid on furfurine, would absorb 8·5 cals. to be realised. It was only natural to enquire if the inverse action could take place. For this purpose, the author tried benzoic aldehyde; as expected, this aldehyde, when heated with chlorhydrate of ammonia to 180—185°, gives off hydrochloric acid gas and water, while chlorhydrate of amarine, easily separated, is formed.

On Chlorated Hydrobenzamide.—M. Delépine.—Chlorated hydrobenzamide is said to be formed by a loss of HCl when chloride of hydrobenzamide is heated to 180—220°, boiling after several rectifications at 187°. Such a low boiling-point seems incompatible with the formula $C_{21}H_{17}ClN_2$; and, in fact, the author found that the oil formed by the distillation of chloride of hydrobenzamide is only a mixture composed of 2 molecules of benzonitrile and 1 molecule of chloride of benzyl, $C_{21}H_{17}ClN_2=2C_6H_5.CN+C_6H_5.CH_2Cl$.

Aromatic Urethanes of Tetrahydroquinolein.—P. Cazeneuve and M. Moreau.—By heating to boiling for two hours 4 molecules of tetrahydroquinolein with 1 molecule of phenolic carbonate, we obtain the phenolic, phenylic orthochlorated, gaïacolic and naphtholic α and β urethanes. Under the same conditions, we have also met with the three cresylic carbonates and carbonate of thymol. By heating tetrahydroquinolein with these carbonates in a sealed tube to above its boiling-point, we should, without doubt, obtain the corresponding urethanes. The authors then go on to describe the methods of preparing and the properties of five urethanes of tetrahydroquinolein they have obtained.

On the Oxazols.—M. Hanriot and G. Reynaud.—When bromoxazolone is treated with warm hydrochloric acid, it easily loses carbonic acid, being transformed into a substituted diethylcetone; only in this case we have a mixture of chlorised and bromised derivatives. A better result is obtained by treating chloroxazolone by hydrochloric acid. If bromoxazolone is dissolved in cold

potash, the solution hardly becomes yellow, notwithstanding that all the bromine is eliminated in the state of bromide of potassium. The strongly alkaline solution precipitates a viscous matter on the addition of an acid, insoluble in water, soluble in alcohol and ether, decomposing at 30° with evolution of carbonic acid. When bromoxazolone is acted on with hot potash, the principal product is a crystalline mass; this is washed first with water, then with a very little ether, and set to crystallise in a mixture of chloroform and ether. Two kinds of crystals are found; the first melt at 182°, while the mother-liquor contains another body fusible at 137°. By heating bromoxazolone with mercury, a similar result is obtained, but the proportion of the body melting at 137° is higher, while very little of the first lot of crystals fusing at 182° is formed.

Some Derivatives of the Aromatic Metadiamines.—M. Jaubert.—A long paper, not suitable for abstraction.

No. 2.

The Reducibility of Metallic Oxides.—H. Hélier.—Already inserted.

On a New Hydrate of the Saline Oxide of Chromium.—G. Baugé.—(See p. 218).

On a New Soluble Antimonic Acid and its Antimoniates.—J. B. Senderens.—By following the instructions given, that is to say, by precipitating the red liquid resulting from the action of nitric acid on trichloride of antimony, with water, we obtain:—1. An antimonic acid, with the formula $Sb_2O_5.nH_2O$, soluble in water. 2. A hydrate, $Sb_2O_5.6H_2O$, produced by the desiccation of the preceding acid freely exposed to the air. 3. The hydrate $Sb_2O_5.3H_2O$, resulting from the desiccation of this latter in the presence of sulphuric acid. 4. Finally, the hydrate $Sb_2O_5.3H_2O$ becomes $Sb_2O_5.2H_2O$, at about 200°; $Sb_2O_5.H_2O$, at about 300°; Sb_2O_5, at about 400°; and this latter gradually changes to Sb_2O_4 when we heat it for a long time to a dull red heat. The author has also prepared a number of antimoniates of nickel, copper, mercury, lead, cadmium, manganese, &c. Many of them, when air-dried, have the formula $Sb_2O_6M.5H_2O$; others contain more water, and resemble the hydrate Sb_2O_5,nH_2O, in which n is greater than 6, and of which the probable existence in solutions of antimonic hydrate has been shown. All these antimoniates, after desiccation in the presence of sulphuric acid, have the general formula $Sb_2O_6M.2H_2O$, corresponding with the antimonic hydrates dried in the same manner, the formula of which is $Sb_2O_5.3H_2O$.

Constitution and Chemical Properties of Ethylidene-imine.—M. Delépine.—The hydrate of ethylidene-imine, as well as the anhydride, have states of polymerisation, of which cryoscopy gives slightly different values; but the existence of a single and unique picrate, obtained indifferently with both substances, points to a single trimerous formula. We must, therefore, consider the aldehydate of ammonia as the hydrate $(CH_3—CH=NH)_3.3H_2O$ of the base $(CH_3—CH=NH)_3$, and the following constitutional formula naturally occurs to one—

The author has applied this formula to a number of experiments, and finds that it not only explains certain known facts, but also adapts itself to new data. These experiments are described at some length.

Action of the *p*-Chlorised and *p*-Bromised Derivatives of Bromomethylphenylcetone on Aniline.—A. Collet.—An alcoholic solution, containing 1 molecule of bromomethyl-*p*-chlorophenylcetone and 2 molecules of aniline, is heated on a water-bath for about a quarter of an hour; on cooling, a yellow crystalline mass separates out; it is but slightly soluble in alcohol, even when warmed. This product is purified by several washings with water to which a little hydrochloric acid has been added, and by crystallisation in a mixture of alcohol and chloroform. In this manner we obtain small bright yellow needles, insoluble in water, slightly so in alcohol, very soluble in chloroform, fusible at about 187—188°, with the composition of a methyl-*p*-chlorophenylcetone anilide, $C_6H_4^{(1)}Cl^{(4)}COCH_2NHC_6H_5$. The action of bromomethyl-*p*-bromophenylcetone on aniline in alcoholic solulution gives an anilide crystallising in pale yellow needles, fusible at 119—120°, insoluble in water, slightly so in alcohol, and very soluble in chloroform.

Methyl-*p*-bromophenylcetone. — A. Collet. — The oxime, $C_6H_4^{(1)}Br^{(4)}C(NOH)CH_3$, was prepared by heating the ketone in alcoholic solution, with an excess of chlorhydrate of hydroxylamine dissolved in a small quantity of water, and previously neutralised with carbonate of soda. It crystallises in alcohol in long colourless needles, slightly soluble in the cold in this solvent, fusible at 128—128·5°. When heated on the water-bath with concentrated sulphuric acid, it is transformed into *p*-bromacetanilide, $C_6H_4^{(1)}Br^{(4)}NHCO.CH_3$, fusible at about 165°.

Methyl-*p*-chlorophenylcetone.—A. Collet.—1 molecule of bromine is added to 1 molecule of methyl-*p*-chlorophenylcetone dissolved in excess of sulphide of carbon or glacial acetic acid; the reaction takes place spontaneously at the ordinary temperature, hydrobromic acid is given off, and the reddish tint of bromine disappears. The solvent deposits crystals fusible at 96°, identical with the product of the action of chloride of bromacetyl on monochlorised benzene in the presence of $AlCl_3$.

The Transformation of the Carbonate of Orthocresol into a Homologue of the Phthalein of Orthocresol. — P. Cazeneuve. — Carbonate of orthocresol, mixed with an excess of soda-lime, heats spontaneously, and undergoes an interesting molecular transposition; it first becomes green and then takes a wine-red colour on the surface through oxidation. The mass, exhausted with water, gives a solution with a fine reddish-violet colour, which is precipitated with HCl, washed, re-dissolved in soda, and re-precipitated. The gelatinous precipitate is dried at a low temperature; it is insoluble in water and benzene, soluble in alcohol, ether, and acetic acid, and will not crystallise.

Action of Phenylhydrazine on Chloranilic Acid.—H. Imbert and A. Descomps.—2·45 grms. of chloranilic acid were dissolved in 150 c.c. of absolute alcohol and poured into 20 c.c. of alcohol containing 2·16 grms. of phenylhydrazine in solution. A very voluminous pearl-grey precipitate is formed, which, under the microscope, shows fine colourless needles. It is washed several times in absolute alcohol, and dried rapidly in vacuo. It gives on analysis C, 50·58; Cl, 16·63; N, 13·87 per cent.

On some Electrolytic Apparatus. — J. Riban. — Several new forms of apparatus are described in this paper, but they cannot be understood without the accompanying diagrams.

The Presence of Di-isopropyl in the Ether of Baku Petroleum. — O. Aschan. — Baku petroleum furnishes, on fractional distillation, a portion boiling at 57—59°, consisting of di-isopropyl, $(CH_3)_2CH.CH(CH_3)_2$. This carbide has been identified with tetramethylethane obtained synthetically by the action of sodium on iodide of isopropyl.—*Ber. der Deut. Chem. Ges.*

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 8th inst., His Grace the Duke of Northumberland, President, presiding. The following were elected Members :—Mr. A. Cooper, F.R.C.S., Mr. A. W. Porter, Mr. S. Stephenson, and Mr. T. Uzielli. The special thanks of the Members were returned to Mr. Hugh Dewar for his donation of £200, to Mr. Thomas H. Sowerby for his donation of £5 5s., and to Mr. John H. Usmar for his donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures. The President referred to the death of Mr. Benjamin Vincent, for many years Assistant Secretary to the Institution, and said that he desired to express the high appreciation that the Managers held of his services.—On Tuesday next, May 16th, Professor W. J. Sollas, F.R.S., will deliver the first of a Course of Three Lectures at the Royal Institution on "Recent Advances in Geology." On Saturday, May 20th, Mr. Edgar F. Jacques will deliver the first of a Course of Three Lectures on "The Music of India and the East, and its Influence on the Music of Europe" (with musical illustrations). And on Thursday, May 25th, Professor L. C. Miall will begin a Course of Two Lectures on "Water Weeds."

New Method for the Preparation of Glycocol.—V. Auger.—Glycocol is generally prepared by Kraut's method, which consists in reacting on monochloracetic acid with a large excess of ammonia, and purifying the product so formed by means of a cupric salt. The author has found it much simpler to react with an alkaline monochloracetate on hexamethyleneamine, molecule for molecule; in such a case it is not necessary to work with dry products. For example, 95 grms. of monochloracetic acid is dissolved in 100 grms. of water, and saturated with a concentrated solution of carbonate of potassium; at the same time add to a solution of commercial formic aldehyde a slight excess of ammonia, and boil to drive off the ammonia. The hexamethyleneamine formed is estimated by evaporating an aliquot part to dryness; mix the two solutions so as to add $1\frac{1}{5}$ molecule of hexamethyleneamine. The temperature rises to about 60°. Evaporate to dryness on a water-bath *in vacuo* for preference. The residue, $(CH_2)_6N_4ClC_2H_2O_2K$, is roughly powdered, and 600 grms. of alcohol at 95° added, and decomposed by the passage of a current of hydrochloric acid gas; formol, chlorides of ammonium and potassium, chlorhydrate of glycocollate of ethyl, and water are formed. The formol is removed by decantation, and the residue washed carefully with alcohol. After distillation, a viscous residue is left; this is diluted with water and boiled with an excess of carbonate of lime and moist oxide of copper. Glycocollate of copper is formed, which is purified and then decomposed by sulphuretted hydrogen. —*Bull. Soc. Chim.*, xxi.-xxii., No. 1.

MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Royal Institution, 3. "Recent Advances in Geology," by Prof. W. J. Sollas, D.Sc., F.R.S.
— Society of Arts, 8. "The Artistic Treatment of Picture Frames," by I. Hunter Donaldson.
WEDNESDAY, 17th.—Society of Arts, 8. "The Law of Trade Marks," by J. E. Evans-Jackson.
— Microscopical, 7.30. Exhibition of Pond Life.
— Institution of Mining and Metallurgy, 8. "The Lucknow (N.S.W.) Goldfield," by A. R. Canning, Assoc.Inst.M.M. "The Silver-Lead Deposits of the Slocan, British Columbia," by J. D. Kendall, M.Inst.M.M. "Notes on the Electro-Deposition of Palladium," by S. O. Cowper-Coles.
THURSDAY, 18th.—Royal Institution, 3. "Embroidery," by Lewis F. Day.
— Chemical, 8. "Corydaline" (Part VI.), by J. J. Dobbie, Ph.D., and A. Lauder. "Oxidation of Furfural by Hydrogen Peroxide," by C. F. Cross, E. J. Bevan, and T. Freiberg.
FRIDAY, 19th.—Royal Institution, 9. "Runic and Ogam Characters and Inscriptions in the British Isles," by The Lord Bishop of Bristol.
SATURDAY, 20th.—Royal Institution, 3. "The Music of India and the East, and its Influence on the Music of Europe" (with Musical Illustrations), by Edgar F. Jacques.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2060.

THE THERMAL EXPANSION OF PURE NICKEL AND COBALT.*

By A. E. TUTTON, B.Sc.

The author has carried out a series of re-determinations of the coefficients of thermal expansion of these two metals with the aid of the interference dilatometer described in a former communication to the Society (*Phil. Trans.*, A, 221, 313; *Roy. Soc. Proc.*, vol. lxiii., p. 208). Since the determinations made by Fizeau in the year 1869, a large amount of additional knowledge has been accumulated with reference to nickel and cobalt, including the discovery of the liquid nickel carbonyl, which places processes of purification in the hands of the chemist of a character so superior to the older methods, as to render it highly desirable that re-determinations of the physical constants of these interesting elements should be carried out with specimens of the metals thus purified. By the kindness of Professor Tilden, who has prepared such specimens with infinite care for the purposes of the investigation of other physical and chemical characters, the author has been enabled to carry out determinations of the thermal expansion with rectangular blocks varying in thickness from 8 to 13 m.m. The blocks were furnished with parallel and truly plane surfaces by the makers of the dilatometer, Messrs. Troughton and Simms. The range of temperature of the observations was from 6° to 121°.

The results of the determinations of the coefficients of linear expansion α are as follows:—

	$\alpha =$	a	$+$	$2bt$
For nickel ..	$\alpha =$	0·000 012 48	+	0·000 000 014 8t
For cobalt ..	$\alpha =$	0·000 012 08	+	0·000 000 012 8t

Nine different determinations were carried out for each metal, three in each of the three rectangular directions, in order to eliminate any slight error due to directional strain in the metallic blocks. As the metals crystallise in the regular system, the expansion should be the same in all directions. The metal in each case had solidified after fusion in an oxy-hydrogen flame in presence at the last of excess of oxygen. The individual results are highly concordant, the highest result for cobalt being still lower than the lowest of the nine values obtained for nickel. Hence there can be no doubt that the above coefficients represent the true relationships.

The main result of the investigation may be summarised as follows:—The coefficients of linear expansion α of pure nickel and cobalt exhibit a slight but real difference; the coefficient of nickel being distinctly greater than that of cobalt. This is true with respect to both the constant a, the coefficient for 0°, and the increment per degree $2b$, of the general expression for the coefficient at any temperature t, $\alpha = a + 2bt$. The difference is consequently one which augments with the temperature; at 0° it amounts to 3·2 per cent, while at 120°, the upper limit of the temperatures of the observations, it attains 4·5 per cent. Similar rules apply naturally to the cubical coefficients. The metal possessing the slightly lower atomic weight, nickel, is thus found to expand to a greater extent than the metal, cobalt, which is endowed with the higher atomic weight.

* Abstract of a Paper read before the Royal Society, May 4, 1899.

ON THE COMPLEX SALTS OF PLATINUM: OXALATES AND NITRATES.

By M. VÈZES.

In a previous paper (*Bull. Soc. Chim.*, xiv., 875) I showed that the plato-oxalates $Pt(CO_2CO_2)_2N_2$, and the chloroplatinites $PtCl_4M_2$ (M representing an atom of a monovalent metal), could be brought to the same general type, that of the plato-salts, PtX_4M_2, this relation being shown by the reactions of double decomposition which—the one in neutral solution and the other in acid—allow these two classes of salts to pass from one to the other. An analogous relation exists between the plato-oxalates and the plato-nitrites, $Pt(NO_2)_4M_2$; it is, in fact, possible to pass from one to the other by the reactions of double decomposition.

These reactions, it is true, are in this case more complicated than in the preceding case, on account of the existence of intermediate bodies, possessing great stability and of very easy formation, while no analogous product appears to be formed in the reaction of the passage of the chloro-platinites into plato-oxalates.

I. *Action of Oxalic Acid on Plato-nitrite of Potassium.*—If we pour into a warm concentrated solution of plato-nitrite of potassium a solution of oxalic acid, in such quantity that the mixture will contain a little more than 1 molecule of acid for each molecule of salt, the solution becomes green, and gives rise to a disengagement of nitrous fumes, which can be accelerated by boiling; when this evolution of gas ceases, the solution takes a golden-yellow tint. It is then left to cool, and an abundant deposit of bright yellow crystals is formed, acting on polarised light. The salt thus obtained has the formula $Pt(CO_2.CO_2)(NO_2)_2K_2+H_2O$, and was formed under these conditions by a regular exchange reaction:—

$$Pt(NO_2)_4K_2+CO_2H.CO_2H = Pt(CO_2.CO_2(NO_2)_2K_2+2NO_2H.$$

This salt, to which we will give the name plato-oxalo-nitrite of potassium, is thus a substitution product of the plato-nitrite, in which two groups $X=NO_2$, derived from the nitrous acid NO_2H, are replaced by the divalent radical $X_2=CO_2.CO_2$, derived from the oxalic acid, $CO_2H.CO_2H$. In its constitution it corresponds to the mixed chloro-nitrated, bromo-nitrated, and iodo-nitrated salts, also very stable in aqueous solution, which I have already described (*Ann. Chim. Phys.*, Series 6, xxix., 145), obtained by the regulated action of hydrochloric, hydrobromic, and hydriodic acids on plato-nitrite of potassium, viz., the plato-dichloronitrate, $PtCl_2(NO)_2K_2$, the plato-dibromonitrite, $PtBr_2(NO_2)_2K_2$, and the plato-diiodonitrite, $PtI_2(NO_2)_2K_2$; this latter has been already obtained by Nilson (*Journ. f. Prakt. Chim.*, Series 2, xxi., 172) by a different method. The reaction of oxalic acid is similar to that of the hydracids, with this difference—that, in view of its bibasicity, a single molecule of acid instead of two takes part in the reaction.

If in this reaction we use a less quantity of oxalic acid than that mentioned above, we still obtain the same salt; but the mother-liquor from the crystallisation, concentrated in its turn, deposits a part of the plato-nitrite unchanged. Thus, under these conditions, it does not form the stable salt with the composition intermediate between that of the plato-nitrite and of the plato-oxalonitrite, and which corresponds to the plato-monochloronitrite $PtCl(NO_2)_3K_2$, and to the plato-monobromonitrite, $PtBr(NO_2)_3K_2$, already described (*loc. cit.*, pp. 178 and 194). The use of an excess of oxalic acid not only prevents the formation of any other mixed salt besides the plato-oxalonitrite, but it also effects the alteration of the appearance of the product obtained. Its colour becomes deeper, passes to brownish-yellow, and then to yellowish-green, without any appreciable change in its composition. The analysis of this green salt, which will be published later on, shows, in fact, that it still possesses, with the

exception of a slight excess of carbon and a very slight deficit of nitrogen, the composition of the plato-oxalonitrite: from this we may conclude that it consists of plato-oxalonitrite, modified in its appearance by its mixture with a little plato-oxalate.

Now, if we act on the plato-nitrite with a large excess of oxalic acid, and if we prolong the action of heat on the mixture, we observe that the liquid becomes brown, and gives, on cooling, simultaneously with this green salt, very fine copper-red needles of plato-oxalate of potassium, $Pt(CO_2.CO_2)_2K_2+2H_2O$, resulting from the exchange reaction—

$$Pt(NO_2)_4K_2+2CO_2H.CO_2H = Pt(CO_2.CO_2)_2K_2+4NO_2H,$$

and corresponding perfectly with the description given by Söderbaum ("Studier öfver Plato-oxalyl föreningar," p. 21; *Thèse Upsal*, 1888) of the deep-coloured isomer of this salt (*Bull. Soc. Chim.*, xix., 876). From this we see, as we should expect, that the plato-oxalate constitutes the final phase of the reaction of oxalic acid on the plato-nitrite. But the elimination of the nitrous acid is difficult to complete, and we always obtain, at the same time as these copper-red needles, greenish crystals of the impure plato-oxalonitrite mentioned above. The separation of these two salts, both only slightly soluble in the cold, is very difficult; at the most we can, by fractional crystallisations in supersaturated solutions, obtain mixtures rich in one or the other of the two salts. From this it results that the reaction just described, although it gives evidence of the relations existing between the plato-nitrites and the plato-oxalates, does not constitute a convenient method for the preparation of the dark coloured plato-oxalate of potassium.

II. *Action of Nitrite of Potassium on Plato-oxalate of Potassium.*—Söderbaum (*loc. cit.*, p. 78; and *Berichte*, xxi., 267, ref. 1888) observed that an excess of nitrite of potassium added to a warm solution of the dark plato-oxalate of potassium, takes away the colour, and on cooling gives a deposit of plato-nitrite. The passage of the plato-oxalate into plato-nitrite is thus effected in neutral solution by the reaction—

$$Pt(CO_2.CO_2)_2K_2+4NO_2K = Pt(NO_2)_4K_2+2CO_2K.CO_2K.$$

I have confirmed this result, but I can further state that it is possible, by using moderate and progressive quantities of nitrite of potassium, to pass, in the inverse order, through all the intermediate stages described in the preceding paragraph; we obtain, in fact, successively the above-mentioned green salt, then the normal plato-oxalonitrite, and finally the plato-nitrite, which is the final phase of the reaction.

Again, while Söderbaum states that the dark plato-oxalate alone is susceptible of the transformation, and that nitrite of potassium is without action on the solution of the pale plato-oxalate, I have observed, on the contrary, that nitrite of potassium acts equally on one and the other of these two isomers. Below, for example, are some analytical data relative to the colourless crystalline product obtained by the action of an excess of nitrite of potassium on the pale plato-oxalate of potassium:—

1. 0·4966 grm. of material, dried in the cold, and not losing any weight after heating for twenty-four hours to 110—120°, was carried to a dull red heat, and under these conditions gave off an abundance of nitrous fumes, and left a residue weighing 0·4289 grm., appearing to consist of platinum and nitrate of potassium: this residue, heated to redness with an excess of sulphuric acid, gave 0·2130 grm. of platinum and 0·1866 grm. of sulphate of potassium, containing 0·0838 grm. of potassium.

2. 0·8678 grm. of the same material, heated to redness with an excess of tungstic acid, gave (after the passage of the gases through heated tubes of copper and oxide of copper) 83·9 c.c. of nitrogen at 0° and 760 m.m. weighing 0·1052 grm.

The pale plato-oxalate of potassium is thus, like the corresponding dark salt, transformable into plato-nitrite by the action of an excess of nitrite of potassium, with this difference, that, even when using a very small quantity of the reagent, we never obtain with the pale plato-oxalate the green salt mentioned above; the only phase of the transition is in this case the normal plato-oxalonitrite. The error here committed by Söderbaum is easy to explain: this plato-oxalonitrite having the same pale yellow colour as the pale plato-oxalate, and being, in a superficial examination, easily mistaken for it. As for the absence of the greenish salt among the products of this reaction, it appears to be explained by the neutrality of the solution; that is a point to which I shall return, as its study appears to lead to the true interpretation of the isomerism of the plato-oxalates.

	Calculated.		Found.	
Pt	194·8	42·60	42·89	—
2K	78·2	17·10	16·88	—
4N	56·2	12·29	—	12·12
8O	128·0	28·01	—	—
$Pt(NO_2)_4K_2$	457·2	100·00	—	—
$Pt+2NO_3K$	369·1	80·71	80·47	—
$Pt+SO_4K_2$	397·1	86·86	86·37	—

It should be remarked that the impossibility of obtaining, in the above-mentioned reaction, any other stable salt with a composition intermediate between the plato-nitrite and the plato-oxalate, except the normal plato-oxalonitrite or its greenish modification, again points to the remarkable stability shown amongst the mixed plato-salts by the compounds of the form $PtX_2Y_2K_2$, a fact pointed out in my previous research (*Ann. Chim. Phys.*, Series 6, vol. xxix., pp. 181, 193, 197, 206), and which Miolati has recently confirmed (*Rendiconti della R. Acad. dei Lincei*, 1896, vol. ii., p. 144).

III. *Other Methods of producing Plato-oxalonitrite of Potassium.*—The relations existing between the plato-oxalates and the plato-nitrites, and notably that which results from the existence of an intermediate plato-oxalonitrite, can be seen by other reactions in which the same salt is formed. It can, in fact, be obtained by the mixture of equal quantities of solutions of the plato-nitrite and the plato-oxalate, the pale variety of this latter salt thus giving rise to the normal oxalonitrite, the dark isomer giving, on the contrary, the greenish salt of almost identical composition.

Further, it is easy to predict, and experiment confirms the fact, that the chloro-, bromo-, and iodo nitrated salts of platinum, of the form $PtX_2Y_2K_2$, will give the oxalonitrite by the same reaction which enables the chlorised, bromised, and iodised salts to pass to the state of oxalate. In this way the action of an excess of neutral oxalate of potassium on the plato-dichloronitrite of potassium, $PtCl_2(NO_2)_2K_2$, gives the normal plato-oxalonitrite—

$$PtCl_2(NO_2)_2K_2+CO_2K.CO_2K = Pt(CO_2.CO_2)(NO_2)_2K_2+2KCl.$$

The inverse passage of the plato-oxalonitrite to the plato-dichloronitrite is also caused just as easily by double decomposition with a metallic chloride capable of forming an insoluble oxalate. In this way the action of the chlorides of calcium, lead, and copper give, with the deposition of the metal in question, a yellow liquor, giving after concentration crystals of plato-dichloronitrite of potassium. We have, for example, in the case of chloride of calcium—

$$Pt(CO_2.CO_2)(NO_2)_2K_2+CaCl_2 = PtCl_2(NO_2)_2K_2+C_2O_4Ca.$$

In the same manner the plato-dibromonitrite and the plato-diiodonitrite have been obtained from the plato-oxalonitrite, one by means of bromide of magnesium, and the other with iodide of lead.

These reactions show that the groups CO_2 of the oxalonitrite play in this body the same *rôle* as the atoms of chlorine, bromine, and iodine in the above mixed salts, and also help to show the analogy of constitution existing

between these three classes of complex salts of platinum—the oxalates, the chlorides, and the nitrites.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No, 4.

ON THE

CHEMICAL REACTIONS INVOLVED IN THE AMALGAMATION OF SILVER ORES.*

By H. F. COLLINS, M. Inst. M.M.

THE experiments of Laur, Huntington, and others have proved that the principal reagents in the patio process are mercury and cuprous chloride.

Most metallurgists appear to have taken it for granted that, as regards the chloride of copper at all events, the reactions taking place in the pan are similar to those of the patio process, and the conclusions of Hague, based on his own experiments, have been accepted without question.

The functions of the iron of the pan itself, together with that existing in the pulp in a finely divided condition, to the amount of 3 to 10 lbs. per ton of ore, and resulting from the abrasion of battery and pan castings, are summed up by both Hague and Egleston as follows:—(1) Direct reduction of AgCl to metal; (2) Reduction of calomel; (3) Direct reduction of Ag_2S; and (4) Reduction of $CuCl_2$ to Cu_2Cl_2; and both agree that the mercury and iron aided by heat and friction are the principal reagents in the extraction of the precious metals in the Washoe process. In the author's opinion, the part played by bluestone in the pan has been very generally misunderstood; the formation of Cu_2Cl_2 can only be accidental and momentary, and all the copper added is reduced to metal almost as soon as it is dissolved. It is indeed well known that practically all the copper added to a pan charge is eventually taken up by the mercury; it does not, however, seem to have occurred to any one to trace the stage at which the copper becomes amalgamated, or to doubt that Cu_2Cl_2 is formed by the action of even a large excess of iron upon $CuCl_2$.

The classical experiment of Hague, upon which so much misconception of the action of copper sulphate has been based, was as follows:—

Two grms. of powdered blende, 1 grm. iron filings, 5 grms. NaCl, 7 grms. $CuSO_45Aq$, were placed in a flask with a little water and kept at 90° C. for a few days. The iron filings rapidly disappeared; metallic copper was precipitated, but re-dissolved probably by the chloride of copper present, the subchloride being formed. Later the iron was thrown down as a basic salt by absorption of atmospheric oxygen. It would appear that Hague, and those who followed him, inferred from this that the Cu_2Cl_2 is formed during amalgamation; but under the existing conditions there are three equivalents of copper present for two of iron, so that there is not sufficient iron present to precipitate the copper, which would require equal equivalents. In investigating the subject the author made the following experiments:—

1. Repeated Hague's experiment in triplicate, leaving out the blende, and, instead of standing for some days, boiled for fifteen minutes, thirty minutes, and two hours respectively, then determined the dissolved copper. The amounts of copper remaining undissolved were respectively 55, 24, and 12·5 per cent of the total amount present.

2. In the presence of free metallic iron in excess, $CuCl_2$ dissolved in excess of NaCl was rapidly reduced to the metallic state. It appears, therefore, that Cu_2Cl_2 in the pan-charge would be almost instantaneously reduced by the large excess of iron present.

3 and 4. A measured quantity of a copper-salt solution was ground with sand in an iron mortar for periods of five and ten minutes. After five minutes' grinding only 6 per cent of the total copper was found to be still soluble in water, and after ten minutes' grinding only 2 per cent, the whole of the remainder having been precipitated. The supposed existence of cuprous chloride in pan pulp is therefore a myth, and the active reagent introduced by the addition of bluestone to the pan-charge is finely divided metallic copper, which soon becomes amalgamated, without, however, losing its power of acting on silver compounds.

A series of experiments was next undertaken with a view to ascertain the relative activities of iron, copper, mercury, and cuprous chloride, in liberating silver from its compounds. In order that the experiments might be made under similar conditions, a shaking frame was prepared to hold six stoppered bottles, into which the silver compounds and the reagents were put.

5. To equal quantities of freshly precipitated AgCl with excess of salt were added equal equivalents of the following substances, and after ten minutes' agitation the excess of AgCl was dissolved in ammonia, and the precipitated silver determined. The results were as follows:—

Reagent added.	Per cent of total Ag precipitated.
1 equivalent of Hg	12·56
1 ,, iron filings ..	28·80
1 ,, copper precipitate	88·50
1 each copper sulphate and iron filings	97·10

As the much more rapid effect of the precipitated copper was judged to be due to its more finely divided state, another experiment (No. 6) was made, by which, to equal weights of freshly precipitated AgCl in excess of salt, equal surfaces of the three metals were exposed for equal times at a boiling temperature. The results were as follows:—

Metallic surface.	Per cent of Ag precipitated.
Mercury	13·2
Sheet iron	91·9
Sheet copper	93·3

These experiments throw light on the well-known fact that docile chloride ores can be treated better, and with less loss of mercury in the iron pan, than in the patio. The results on sulphide ores are, however, known to be different, and the next series of experiments on an artificial mixture of sand and silver sulphide was made to investigate this difference.

7. Silver sulphide was ground with excess of sand, mercury, salt, and the following special reagents in a Wedgwood mortar, and the silver, reduced to the metallic state, determined by taking up with mercury, panning off, and retorting. The mean results of eight sets of experiments were as follows.—

Special reagent added.	Per cent of Ag reduced to metal.
Iron filings	2·60
Precipitated copper ..	5·99
Cuprous chloride	7·62
Cu_2Cl_2 and iron filings ..	10·66
$CuSO_4$ and iron filings ..	3·20
None	2·00

The above experiments not seeming to point to any definite conclusion beyond proving that cuprous chloride has a more powerful effect than metallic copper or iron, another set of experiments was made in bottles contained in the shaking frame.

8. To equal quantities of silver sulphide were added excess of mercury and salt, and the special reagents mentioned below. The total time of contact was eighty hours, of which twenty-six hours was at the boiling temperature with constant agitation. The results were:—

* Abridged from a Paper read before the Institution of Mining and Metallurgy, April 19th, 1899.

Special reagent added.	Per cent of Ag reduced to metal.
Iron filings	32·8
Copper precipitate (fresh)	37·0
Cu_2Cl_2 and copper filings	72·3

This experiment confirms the former, and shows clearly that the effect of metallic copper upon Ag_2S, though more powerful than that of iron, is less powerful than that of Cu_2Cl_2. This explains the rooted aversion which patio and fondo amalgamators have to the use of iron in grinding unless counterbalanced by a comparative enormous subsequent excess of bluestone, and the undoubted fact that on raw sulphide ores the patio or fondo will extract a better percentage than the pan in which the addition of bluestone, in even large amount, can only result in the formation of metallic copper, but, as already shown, never in that of the more active Cu_2Cl_2.

The conclusions which may be drawn from a consideration of the above experiments are the following:—

1. When treating "chloride" silver ores, the iron pan will give at least as perfect an extraction as the patio, with far less loss of mercury, owing to the fact that the affinity of iron for the chlorine combined with the silver is so much greater than that of mercury (Expts. 5 and 6).

2. When treating such ores in the pan, the reactions are not sufficiently accelerated by the use of bluestone to compensate for the increased cost. Similarly, the increase in rapidity by the substitution of the copper fondo for the iron pan does not justify the increased cost (Expt. 6).

3. When treating sulphide ores, however, the extraction is much accelerated and increased by the addition of bluestone (Expts. 7 and 8).

4. The bluestone, when added to the pan-charge, is very speedily reduced to metal. The copper so precipitated amalgamates with the mercury, and acts upon silver sulphide more energetically than either metallic iron or mercury, or both combined (Expts. 7 and 8). No cuprous chloride is formed in the pan, or, if formed temporarily by the secondary action of precipitated copper upon undecomposed cupric chloride, it is reduced to metal by the excess of iron present, long before it can exercise any effect upon the silver sulphide present (Expts. 1 to 4).

5. That nevertheless cuprous chloride has a still more powerful effect upon Ag_2S than metallic copper, however freshly precipitated (Expts. 7 and 8).

6. That this powerful effect of Cu_2Cl_2 explains the observed fact that upon raw or badly roasted sulphide ores, the fondo (in which Cu_2Cl_2 is constantly regenerated for re-use, gives a better extraction than the *pan* (in which Cu_2Cl_2, if accidentally formed, is almost at once decomposed).

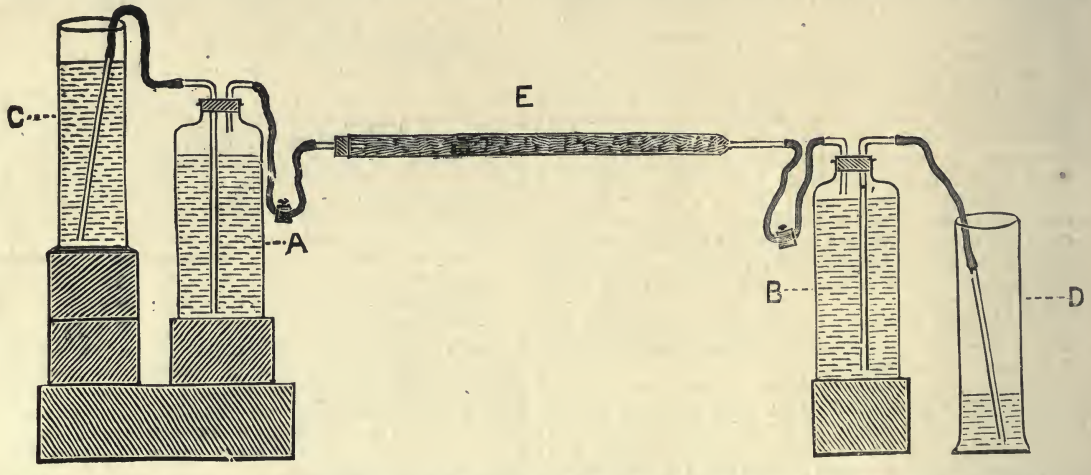
Anticipating criticism of these experiments as unpractical on the ground that they refer to processes which are either obsolete or rapidly becoming so, the author thinks it well to recall the fact that over one-fourth of the world's total output of silver is still produced by amalgamation processes, which in countries where the ores and conditions are suitable—as in parts of Mexico, Columbia, Bolivia, and Peru—are likely to hold their own as against smelting processes for at least another century to come.

LABORATORY NOTES.

By W. FRENCH and J. M. BROTHERS.

Volume Composition of Carbon Monoxide.

The accompanying sketch will explain a method used here for class work, and which has given satisfactory results. A and B are two syphon bottles with the syphon-tubes dipping into C and D respectively by rubber and glass tubing. The liquid in the four vessels is water previously saturated with carbon dioxide gas. Carbon dioxide is passed into A until it is about one-third full; it is then connected to the combustion-tube E, containing



scrap charcoal (recently ignited), and the air replaced by CO_2 from A. B, which is quite filled with CO_2 water, is now connected to the other end of E, the syphon-tube filled and dipped into D. The tube E (about 2 feet long) is now heated in a combustion furnace; when the charcoal is red-hot, A and C are raised whilst B and D are lowered (C being higher than A, and D being lower than B), the gas slowly passing from A to B; when all the gas has passed over to B, the levels of the bottles are reversed and the gas is passed back to A.

The process is repeated about four times and cooled. The volume is then found to have been doubled, and readily proved to be carbon monoxide. The same apparatus, having copper in the tube E, is also used to determine the volume composition of the oxides of nitrogen. Three or four students working together may easily perform the experiment, and it possesses advantages over the use of mercury and sodium for elementary students.

Bury Grammar School.

Physical Society.—Owing to the resignation of Mr. Appleyard, Mr. R. W. Forsyth has been appointed Reporter to the Physical Society of London.

THE CONSTITUTION OF THE AMMONIUM-MAGNESIUM PHOSPHATE OF ANALYSIS.*

By F. A. GOOCH and MARTHA AUSTIN.

In a recent paper from this laboratory (*Am. Journ. Sci.*, vi., 233) it has been shown that the presence of ammonium chloride or other ammonium salt is necessary in the precipitation of manganese as the ammonium-manganese phosphate by microcosmic salt in order that the precipitate may have the ideal constitution represented by the symbol NH_4MnPO_4.

It was also shown that the solvent effect of the ammonium chloride upon the precipitated ammonium-manganese phosphate is not marked when an excess of the precipitant is present in solution.

The relations disclosed in this paper suggest that the chemical constitution of the precipitate rather than mechanical contamination and varying solubility—the explanations generally accepted, and, indeed, advocated by one of us in a former paper (*Am. Chem. Journ.*, i., 391)—may be responsible for observed variations in the weight of the residue derived by the ignition of the similar salt of magnesium, the ammonium-magnesium phosphate, precipitated by an excess of a soluble phosphate from the solution of a magnesium salt, or from the solution of a soluble phosphate by an excess of a magnesium salt.

Precipitation by Excess of the Soluble Phosphate.

The precipitation of the magnesium salt by an excess of the soluble phosphate was first studied. For this work a solution of pure magnesium nitrate was prepared by dissolving the pure magnesium oxide of commerce in a slight excess of pure hydrochloric acid and boiling with more magnesium oxide. After filtering off the excess of magnesium oxide and any trace of iron or members of the higher groups, the solution was precipitated by ammonium carbonate, the precipitate was washed by repeated boilings and filtrations until silver nitrate gave no precipitate in the solution acidified with nitric acid. This precipitated carbonate was nearly dissolved in nitric acid, and the solution was boiled with an excess of the carbonate (for the purpose of removing traces of barium, strontium, and calcium), filtered, and diluted to definite volume. The evaporation of a definite volume of the solution and strong ignition of the residue would be a most natural method of establishing a standard of the solution, were it not for the fact pointed out by Richards and Rogers (*Am. Chem. Journ.*, xvi., 567) that the oxide of magnesium retains on ignition occluded nitrogen and oxygen enough to increase its weight sensibly. For this reason the nitrate was converted to the sulphate and weighed as such—either by evaporating to dryness in a weighed platinum crucible a definite volume of the solution, igniting as oxide, and changing to the sulphate by heating with sulphuric acid; or, by evaporating the magnesium nitrate directly with an excess of sulphuric acid of half strength. In this treatment the excess of acid was removed by heating the platinum crucible upon a porcelain ring or triangle so placed within a porcelain crucible that the bottom and walls of the inner crucible were distant about 1 c.m. from the bottom and walls of the outer crucible. The excess of acid is easily removed in this way, and the outer crucible may be heated to redness without danger of breaking up the magnesium sulphate. The results of this work, taking O = 16, Mg = 24·3, N = 14·03, S = 32·06, are given in the accompanying table.

The magnesium oxide obtained by direct ignition of the nitrate weighed on the average about 0·0010 grm. more than the oxide theoretically present in the weighed sulphate from equal portions of the solution.

Table I.

$MgSO_4$ obtained by converting ignited MgO into the sulphate.	$MgSO_4$ obtained directly from 50 c.m.³ $Mg(NO_3)_2$.	Theoretical amount of MgO in $MgSO_4$.
Grm.	Grm.	Grm.
0·5748	—	0·1924
0·5739	—	0·1923
—	0·5741	0·1922
—	0·5750	0·1925

Before proceeding to study possible chemical effects of ammonium chloride in determining the constitution of the ammonium-magnesium phosphate, it is obviously necessary to define the extent to which the ammonium salt may exert a solvent action in presence of the precipitant. Fresenius estimated that ammonium-magnesium phosphate is soluble in 15,293 parts of cold water, but the method of investigation employed did not entirely preclude the possibility of counting as ammonium-magnesium phosphate soluble material included and held in the original precipitate ("Fresenius," 6te Aufl., p. 805). According to Kissel (*Zeit. Anal. Chemie*, viii., 173), the phosphate, which dissolves in a mixture of ammonia and water in the proportion of 0·0040 grm. to the litre and in the proportion of 0·0110 grm. to the litre in a similar mixture containing also 18 grms. of ammonium chloride, is practically insoluble in the latter mixture if an excess of magnesia mixture be added; and Heintz (*Zeit. Anal. Chemie*, ix., 16) showed that the effect of adding an excess of sodium phosphate in the solution is similar.

So far as appears, no quantitative experiments have been recorded in which the behaviour of a mixture of ammonium chloride and magnesium salt and an insoluble phosphate in a solution only slightly ammoniacal has been tested, though as a matter of convenience the use of faintly ammoniacal solutions and faintly ammoniacal wash-water is to be preferred to the mixture of strong ammonia and water (1 : 3) ordinarily employed. As a preliminary step, therefore, in the work to be described, experiments were made to find how small an amount of magnesium could be detected in solution by precipitating with microcosmic salt, either alone or in presence of ammonium chloride in faintly ammoniacal solutions. The ammonium chloride used for these tests (as well as in the similar quantitative work following) was purified by boiling with a faint excess of ammonia, filtering, digesting twelve hours with microcosmic salt, and filtering again. The results are given in Table II.

Table II.

Weight of MgO taken as the nitrate. Grm.	$H(NH_4)NaPO_4 4H_2O$ taken. Grms.	Volume. C.m.³.	NH_4Cl taken. Grms.	Opalescent precipitation.
0·0003	1·75	100	—	Marked.
0·0003	1·75	500	—	,,
0·0003	1·75	100	10	,,
0·0003	1·75	500	10	,,
0·0003	1·75	500	30	Faint.
0·0001	1·75	100	—	Marked.
0·0001	1·75	100	10	,,
0·0001	1·75	500	10	Faint.
0·0001	1·75	500	60	,,

The results of these tests show that even so little as 0·0001 grm. of magnesium oxide may be detected in 500 c.c. of faintly ammoniacal water containing as much as 60 grms. of ammonium chloride.* It is plain that strongly ammoniacal liquids are entirely unnecessary in the precipitation of the ammonium-magnesium phosphate under the conditions. In nearly all the experiments to be detailed use was made, therefore, of faintly ammoniacal solutions and wash-water.

(To be continued).

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Series 4, vol. vii., No. 39, March, 1899.

* It was found also, incidentally, that the presence of reasonable amounts of ammonium oxalate (100 c.m.³ of the saturated solution) does not interfere with the precipitation of the ammonium-magnesium phosphate by microcosmic salt.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 4th, 1899.

Professor THORPE, F.R.S., President, in the Chair.

MESSRS. David Hooper and W. H. Mills were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry Meldola Danziger, Clent House, Woodland Road, Northfield, Birmingham; William Gordon Fraser, Golspie, St. Albans; Henry Royal-Dawson, 3, Kenilworth Road, Ealing, London, W.; Samuel Stansfield, White Lee, Mytholmroyd, Manchester; Christopher Joseph Whittaker, Willow House, Blackburn Road, Accrington.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

James Herbert Allworthy, Peter Auchinachie, Clement Harrison Baker, Frederick James Beale, Frank Belton, Benjamin Harvey Bennetts, Alfred Ernest Bond, George Smith Bratby, Kendall Colin Browning, B.A., William Collingridge, M.A., Robert D. Connell, Charles Robert Darling, Harold Francis Carl Goltz, Percy Haigh, John Elias Hughes, Archibald Glen Kidston Hunter, Lauder William Jones, B.A., Ph.D., Thomas Judge, B.A., Robert William Lindsey, James MacLeod, William McConnell, Wilfred Walter Morris, Laurence C. Panting, B.A., M.B., Frederick Williams Pittuck, Harold McLean Read, S. B. Schryver, D.Sc., Ph.D., Maurice Emile Schweich, Edward Thomas Shelbourn, Arthur John Shelton, Harry Alexander Thiersch, Robert Tatlock Thomson, Richard Threlfall, Ernest Albert Tyler, B.A., Arthur Luvian Wade, Allan Frederick Walden, M.A., Charles Walker, Fred Sheasby Watson, B.Sc.

Of the following papers those marked * were read:—

*60. "*On the Combustion of Carbon Disulphide.*" By HAROLD B. DIXON and E. J. RUSSELL.

The authors have investigated the temperature of ignition of carbon disulphide in air, its stability on heating, its mode of burning in air in the divided flame, and its explosion with oxygen.

Experiments on the ignition point of carbon disulphide showed considerable variations. It was found that the vapour undergoes a phosphorescent combustion in air similar to that of phosphorus, sulphur, ether, &c. This phosphorescence is well seen in a dark room when the vapour impinges on a glass vessel at 230°. The lowest temperature at which actual ignition was observed was 232°. Carbon disulphide distilled in a current of nitrogen through a porcelain tube heated to 400° showed no visible decomposition. When carbon disulphide was sealed up in a glass tube and submitted to prolonged heating at 230°, a slight yellow film formed on the glass. A similar film was produced by the prolonged action of bright light.

Although carbon disulphide is decomposed by a violent shock (*e.g.*, an explosion of fulminate) into its elements, this decomposition is not propagated through its vapour as an explosion, but dies out. When carbon disulphide is exploded with defect of oxygen, it does not yield a deposit of carbon. When it is exploded in a long tube with an excess of oxygen, the products of the combustion are mainly those required by the equation $CS_2+3O_2=CO_2+2SO_2$, but there are always present small quantities of carbon disulphide, oxysulphide, and monoxide with the excess of oxygen.

When carbon disulphide is exploded in a long tube with insufficient oxygen for complete combustion, the products are carbon dioxide and sulphur dioxide along with carbon oxysulphide and monoxide, sulphur, and unchanged carbon disulphide. As the oxygen is gradually diminished, the amount of sulphur dioxide falls off, whilst the carbon monoxide increases. The authors were unable to set up the explosion-wave in mixtures containing less than 40 per cent of oxygen. So far as the experiments could be carried, there was always a division of the oxygen between the carbon and sulphur. No simple equation expresses the mode of burning. In the incomplete combustion of carbon disulphide, the sulphur was deposited partly in the "liquid" condition.

The maximum velocity of the explosion-wave was found when the oxygen just sufficed for complete combustion.

When carbon disulphide vapour and air are burnt as the Smithells divided flame, the products of the inner flame are sulphur dioxide and carbon monoxide in nearly equal volumes, some unchanged carbon disulphide, and only small quantities of carbon dioxide and oxysulphide.

DISCUSSION.

Professor TILDEN said that it seemed to him impossible to determine or to state exactly the temperature of ignition of any combustible substance, inasmuch as this depends largely upon conditions such as the proportion of air present, and especially the extent of the heated surface by which the action is started. As an example, the very small, though very hot, sparks from a flint and steel are known to be incapable of inflaming a mixture of coal-gas and air, while a red-hot iron-bar, though at much lower temperature, does cause ignition by reason of its greater mass,

Dr. WYNNE said that in purifying carbon bisulphide for the purpose of determining its magnetic rotation, the late Mr. Rodger, by exposing the liquid to sunlight, had obtained some quantity of the brown substance with a view of determining its composition. The prevalent idea seemed to be that the brown substance was a sub-sulphide, possibly C_2S_3, and it would be interesting to know whether Professor Dixon had any evidence bearing on the point.

Professor SMITHELLS said that he could confirm Professor Dixon's remark as to the phosphorescent combustion of carbon disulphide. This substance might be added to the long list of carbon compounds which were capable of phosphorescent combustion. The combustion of carbon disulphide was of special interest from the fact that the flame did not exhibit the so-called carbon or candle spectrum, but this he believed could be explained by the masking effect of the burning sulphur. He had found that a burning mixture of ethylene and hydrogen sulphide gave no carbon spectrum, although an ethylene air flame of itself would of course do so. He had made some examination of the partial products of combustion of carbon disulphide; they were difficult to deal with, and he was glad that Professor Dixon had brought the inquiry to a successful issue. It was interesting to remark that some years ago Julius, from an examination of the spectrum of burning carbon disulphide, had concluded that some third substance besides carbon dioxide and water was formed, and he had detected carbon oxysulphide. Professor Dixon, however, had gone much further in establishing this fact.

*61. "*The Action of Nitric Oxide on Nitrogen Peroxide.*" By HAROLD B. DIXON and J. D. PETERKIN.

Some few years ago, the question was keenly debated whether nitrogen trioxide existed in the gaseous state. On both sides, the final appeal was made to the behaviour of nitric oxide when mixed with gaseous nitrogen peroxide. Ramsay and Cundall (*Trans.*, 1895, lxvii., 672) broke an inner tube, containing nitric oxide over mercury, by pressing it against an outer tube containing the peroxide over mercury. No contraction was observed. The experiment proved that no considerable quantity of trioxide could have been formed on mixing the gases. Lunge and Porschnew (*Zeit. Anorg. Chem.*, 1894, vii., 209) broke a thin glass diaphragm between a vessel containing nitric oxide and a similar one containing the peroxide. The gases showed a very slight expansion on diffusing "instead of

the large contraction expected." The natural conclusion of chemists has been that "gaseous N_2O_3 appareutly does not exist."

But the dissociation which nitrogen peroxide undergoes on diminution of pressure would have caused an appreciable expansion in these experiments if the nitric oxide had merely played the part of an inert gas.

The authors confirm Lunge and Porschnew's conclusion that a very slight alteration of volume occurs on mixing nitric oxide with the peroxide at 27°, but they show that a considerable expansion occurs when the peroxide mixes with nitrogen and other inert gases, and that this observed expansion is in close agreement with that calculated from Willard Gibbs's formulæ for the dissociation of the peroxide. The authors infer from their experiments that at 27° nitric oxide and peroxide combine to a limited extent to form an unstable compound, which is largely dissociated at this temperature, and undergoes increasing dissociation as the temperature is raised. The reversibility of the equation $N_2O_3 = NO + NO_2$ affords an easy explanation of the behaviour of the mixed gases towards reagents.

Discussion.

Professor Ramsay congratulated Professor Dixon on having shown that in the gases evolved from nitrous anhydride, which consist chiefly of a mixture of nitric oxide and peroxide, a small amount of gaseous nitrous anhydride is to be detected. The power of this mixture of gases to react as N_2O_3 is thus explained. In 1885, he (Professor Ramsay) stated that, as the result of experiments showing that, in the main, the gases obtained from liquid anhydride consist of NO_2, N_2O_4, and NO, "it cannot be taken as conclusive that no nitrous anhydride is present in the gaseous state"; and Professor Dixon has found that a small proportion does so exist. The proof is valuable, inasmuch as it explains why the mixture of gases can act on sulphuric acid, be absorbed by soda, and act as a diazotising agent.

Professor Dewar said that, in his paper, "Studies on the Electric Arc" (*Proc. Roy. Soc.*, 1880, xxx., 85) experiments are described showing the amount and character of the oxides of nitrogen produced when an arc is maintained in a cool dry moving atmosphere. The quantity of oxides formed did not exceed 1 grm. per hour. As the solution of the oxides in concentrated sulphuric acid gave the same percentageof nitrogen whether treated directly with mercury or after careful dilution with water and subsequent titration of the solution with permanganate, it was inferred that the main product was gaseous nitrous anhydride.

Experiments are also described in an address on "Phosphorescence and Ozone" (*Proc. Roy. Inst.*, 1888, xii., 557), which have an important bearing on this question. A current of attenuated air was maintained in a small vacuum tube of the ordinary form, and after the passage of the electric discharge was allowed to expand into a glass cylinder 3 feet long and 6 inches in diameter, maintained at a pressure not exceeding 6 or 8 m.m. by means of a large air-pump. The result was the production of extraordinary phosphorescent effects in the stream of air. This phosphorescence is associated with the production of ozone and oxides of nitrogen, as it does not take place in the absence of oxygen. Recently, the phosphorescent glow was allowed to pass through some liquid air in order to condense and solidify the oxides of nitrogen and dissolve the ozone out of the moving, luminous gas stream. The result was that the clear liquid air soon became turbid from the formation of a precipitated greenish-blue solid. On filtering this off, it gave all the reactions of nitrous acid, and no ozone was found in solution. The colour of the body at the low temperature shows it was not N_2O_4, which is colourless. It might be, however, a mixture of nitric oxide and nitrous anhydride. On the other hand, it is possible that NO_2, the dissociated molecule of N_2O_4, may exist in the solid state at a very low temperature and be coloured.

Mr. C. E. Groves said that, many years ago, in the course of experiments on the preparation of nitrosyl sulphate, he had found that the brown vapours given off when arsenious anhydride was heated at 70° with nitric acid of sp. gr. = 1·3 were almost entirely absorbed by concentrated sulphuric acid. Crystalline nitrosyl sulphate was formed, and but little, if any, nitric acid, although the latter should have been produced if nitric peroxide had been present. More recently, he had observed that these same vapours, when passed into a mixture of crushed ice and water, were absorbed, forming a solution of nitrous acid.

Professor Tilden said it was generally acknowledged that nitrogen trioxide existed only in the form of the blue liquid, which becomes almost completely dissociated by vaporisation. Professor Dixon seemed to have proved that in this case, as in so many others, a dissociable compound is more stable in the presence of the products of its dissociation.

*62. "*On the Mode of Burning of Carbon.*" By Harold B. Dixon.

In the combustion of carbon, the formation of carbon dioxide is usually described as being due to a single and direct action between carbon and oxygen; it is stated or implied that carbon monoxide is only formed by a secondary action between carbon dioxide and carbon. The only experiments which claim to prove this are the two series made by Julius Lang (*Zeit. Phys. Chem.*, 1888, ii., 168).

The author repeated Lang's experiments, and found that when oxygen was passed over carbon heated to 500° (a temperature at which Lang showed carbon dioxide was not reduced by carbon), even in a very slow stream, some carbon monoxide was always formed.

Under conditions far less favourable for the reduction of carbon dioxide than in Lang's experiments, viz., by passing a mixture of carbon dioxide with 6—8 per cent of oxygen over carbon heated to 500°, some carbon monoxide was always formed.

Lang's more important argument depends on his second series of experiments, which consisted in passing a mixture of oxygen, carbon monoxide, and nitrogen over carbon at 500°. He found that with a slow stream, the carbon monoxide remained unchanged in amount, whilst all the oxygen was converted into carbon dioxide; with a quicker stream, the proportion of carbon monoxide increased considerably, but with a still quicker stream it was much reduced. The author has made many experiments to test these results. When a mixture containing about 80 per cent of oxygen and 20 per cent of carbon monoxide, was passed quickly over coke heated to 500°, the blue flame of burning carbon monoxide was observed, and the amount of that gas found in the products was small. On lowering the rate of the gas stream, the flame was not formed, but the carbon glowed and the amount of carbon monoxide in the products increased. This reached a maximum and then diminished as the rate of the stream was continually lowered. With a very slow stream, from 2—4 per cent of carbon monoxide was found in the products. These results are quite opposed to the conclusions drawn by Lang, viz., that carbon monoxide is unaltered when mixed with oxygen, it is passed very slowly over carbon at 500°. His argument that carbon dioxide must be first formed is therefore invalid.

The results of the new experiments might be explained on either hypothesis if it be assumed that the molecule of the monoxide, or of the dioxide, as the case may be, formed by the direct union of the elements at 500°, retains sufficient heat (from its heat of formation) to react with oxygen or carbon respectively. The experiments of Baker (*Phil. Trans.*, 1888, clxxix. A, 571), make it very probable that the carbon burns first to carbon monoxide.

Discussion.

Professor Clowes said that Haldane (*Trans. Inst. Mining Engineers*, xvi., 470), had shown that a small pro-

portion of carbon monoxide accompanied carbon dioxide in the products of the spontaneous oxidation of coal at ordinary temperatures. The carbon monoxide was detected by the reaction with diluted blood, its proportion was estimated by this colorimetric method, and the result confirmed by the ordinary gasometric method.

*63. "*Crystalline Glycollic Aldehyde.*" By Henry J. Horstman Fenton and Henry Jackson.

It has previously been shown by one of the authors (*Trans.*, 1895, lxvii., 774), that dihydroxymaleic acid, when heated with water, breaks up almost quantitatively into glycollic aldehyde and carbon dioxide, $C_4H_4O_6 = C_2H_4O_2 + 2CO_2$.

The resulting solution, after purification by treatment with calcium carbonate and extraction with alcohol, yields on evaporation in a vacuum, a colourless, sweet syrup, which was shown to be the aldehyde in nearly a pure state. Traces of the solvent used for purification, however, are obstinately retained, and various attempts have been made to obtain the substance absolutely pure.

It was further shown (*Trans.*, 1897, lxxi., 375) that this syrup, when heated to 100° in a vacuum, polymerises to a large extent, giving a hexose, $C_6H_{12}O_6$. During this operation, a small quantity of crystalline substance was often observed in the exit tube of the apparatus employed, but the quantity was too minute for thorough examination. By taking certain precautions, the authors now find that this crystalline substance can be obtained in fair quantity, that it is invariably produced in the process referred to, and on examination proves to be pure glycollic aldehyde.

Molecular weight determinations by the cryoscopic method indicate that, in the crystalline state, the substance is probably bimolecular, the numbers obtained when the solution is first made approximating to those required for the double formula, $C_4H_8O_4$. But on allowing the solution to stand, this value diminishes, and, after about 24 hours, becomes constant, and agrees almost exactly with that required for the single formula. This behaviour is quite analogous to that which Wöhl observed in the case of crystalline glyceraldehyde (*Ber.*, 1898, xxxi., 2394).

*64. "*On the Blue Salt of Fehling's Solution and other Cuprotartrates.*" By Orme Masson and B. D. Steele.

In this paper, electrolytic and chemical experiments are described which prove (*a*), that the blue salt contains a complex negative radicle of which copper is a part; (*b*), that none of the copper plays an electropositive part; (*c*), that when a current passes through the blue solution, copper is deposited on the cathode by secondary action of the *K* ions there; (*d*), that the blue solution may be prepared perfectly neutral to litmus by the interaction of cupric tartrate and alkali in the ratio of 5KOH to $4CuC_4H_4O_6$, and that this neutral solution contains $K_2C_4H_4O_6$ as well as the blue salt; (*e*), that the latter may be completely purified by precipitating it with alcohol; (*f*), that when dried in vacuo it has the composition $K_3C_{12}H_9Cu_4O_{19},4H_2O$; (*g*), that it gives rise to the production, by double decomposition, of a series of salts of the heavy metals, obtained as more or less insoluble, blue, amorphous precipitates, of which the silver and lead salts have been analysed; (*h*), that the free acid corresponding to these cuprotartrates is unstable and, so far, unobtainable; (*i*), that excess of alkali converts the neutral blue cuprotartrate into a strongly alkaline salt, which is also capable of being separated by alcohol.

Discussion.

Dr. Thorne said the blue salt has been recently examined in his laboratory by his assistant, Mr. E. H. Jeffers. It had been obtained by precipitation as a viscid liquid gradually depositing crystals, but it had not yet been isolated in a pure state. It was readily soluble in water, and the aqueous solution did not show any decomposition on boiling.

It is remarkable that the whole of the copper should be present in the negative condition. The complicated formula assigned to the salt seemed improbable, as Luff has recently (*Zeits. Ges. Brauw.*, 1898, xxi., 319) described a potassium cupric citrate, $K_2Cu(C_6H_4O_7),6H_2O$, obtained in an analogous way. This latter salt appears to be an ordinary double salt with the copper in the positive condition, but its behaviour with reducing sugars is similar to that of the tartrate described.

*65. "*The Preparation of Acid Phenolic Salts of Dibasic Acids.*" By S. B. Schryver, D.Sc., Ph.D.

When the sodium salt of a phenol is treated with the anhydride of an organic dibasic acid in the presence of a liquid, such as a hydrocarbon, which exerts no chemical action on either the phenol sodium salt or the anhydride, a reaction takes place, which may be represented by the following general equation:—

$$R{<}\begin{matrix}CO\\CO\end{matrix}{>}O + XONa = R{<}\begin{matrix}COOX\\COONa'\end{matrix}$$

where R = residue of an organic dibasic acid, X = a phenylic group.

The hydrocarbon most generally employed was xylene. The phenol was dissolved in about ten times its weight of the hydrocarbon, and the sodium salt prepared by the direct action of metallic sodium on this solution. On adding the anhydride, an immediate action takes place in most cases, and the sodium phenolic salt separates out on standing in the form of a gelatinous mass. This can be dissolved up in water and thus separated from the hydrocarbon, and the acid phenolic salt can be precipitated from the aqueous solution of the sodium salt thus obtained by the addition of dilute mineral acids. By means of the reaction, the following substances were prepared:—

Phenol hydrogen camphorate—
$CO_2H{\cdot}C_8H_{14}{\cdot}CO_2(C_6H_5)$, m. p. 100°.

Thymol hydrogen succinate—
$CO_2H{\cdot}C_2H_4{\cdot}CO_2(C_{10}H_{14})$, m. p. 121—122°.

Thymol hydrogen phthalate—
$CO_2H{\cdot}C_6H_4{\cdot}CO_2(C_{10}H_{14})$, m. p. 132·5°.

Thymol hydrogen camphorate—
$CO_2H{\cdot}C_8H_{14}{\cdot}CO_2(C_{10}H_{14})$, m. p. 89°.

Guaiacol hydrogen succinate—
$CO_2H{\cdot}C_2H_4{\cdot}CO_2(C_6H_4{\cdot}OCH_3)$, m. p. 75°.

Guaiacol hydrogen camphorate—
$CO_2H{\cdot}C_8H_{14}{\cdot}CO_2(C_6H_4{\cdot}OCH_3)$, m. p. 112°,

from which the neutral salt, $C_8H_{14}(CO_2C_6H_4{\cdot}OCH_3)_2$, m. p. 124°, was prepared, β-Naphthol hydrogen camphorate, $CO_2H{\cdot}C_8H_{14}{\cdot}CO_2C_{10}H_7$, m. p. 120—121°. Eugenol hydrogen camphorate, m. p. 115·5°. Carvacrol hydrogen camphorate, a syrup.

As will be seen from the above examples, the reaction is applicable to a large number of phenols and acid anhydrides, but it does not apply, however, universally. So far, two classes of exceptions have been discovered amongst substituted phenols.

(1). The ortho- and para-nitrophenols.—Whereas the sodium salt of metanitrophenol dissolves readily in a 10 per cent solution of camphoric anhydride in xylene, neither the corresponding ortho- nor para-compounds react, even when heated to 180° in a sealed tube. Reference is made to the differences in the reaction of meta-compounds, as opposed to the corresponding ortho- and para-compounds, in the publications of Menschutkin (*Ber.*, 1897, xxx, 2968) and Lobry de Bruyn (*Rec. Trav. Chem.*, 1894, xiii., 101—147). The metanitrophenol camphorate, $CO_2H{\cdot}C_8H_{14}{\cdot}CO_2C_6H_4{\cdot}(NO_2)$, prepared by the reaction, commences to melt at 115°, but is not completely molten till some degrees higher.

(2). Diortho-substituted phenols.—A series of bromo-compounds was prepared, viz., *p*-bromophenol, 2 : 4-dibromophenol, 2 : 6-dibromophenol, 2 : 4 : 6-tribromophenol. 2 : 6-Dibromophenol was obtained by the reduction of 2 : 6-dibromoparanitrosophenol (OH = 1) and subsequent replacement by hydrogen of the amino-group

in the product thus obtained by means of ethyl nitrite. The other bromophenols were obtained by direct bromination.

It was found that, whereas *p*-bromophenol and 2 : 4-dibromophenol readily reacted with camphoric anhydride yielding camphorates, $CO_2H{\cdot}C_8H_{14}{\cdot}CO_2C_6H_4Br$, and $CO_2H{\cdot}C_8H_{14}{\cdot}CO_2C_6H_3Br_2$, melting respectively at 111° and 173°, neither the 2 : 6-dibromophenol nor the 2 : 4 : 6-tribromophenol reacted, even when heated to 180° in a sealed tube. This non-reactivity is analogous to the non-formation of alkyl salts of diortho-substituted benzoic acids (compare V. Meyer and Sudborough, *Ber.*, 1894, xxvii., 510, 512, 1580, 3146). V. Meyer ascribes the non reactivity to stereochemical causes. In this case, as well as in the reactions described above, it seems doubtful whether the non-reactivity is to be ascribed to the presence merely of two substituted groups in the ortho-position (stereochemical causes), or to the close proximity of two strongly negative groups—in other words, to statical or dynamical causes—especially when the fact is taken into account that even certain mono-substituted products are incapable of reacting.

Discussion.

Dr. Lapworth thought that Dr. Schryver's observations afforded further evidence in favour of the view that in the salts of ortho- and para-nitrophenols the constitution of the nucleus is no longer benzenoid, but quinonoid; that is to say, that the salts are derivatives of isonitro-compounds analogous to quinoneoximes, and not to true phenols. In the case of metanitrophenol, as the migration of the phenolic hydrogen into the nitro-group is not possible, and as nitrobenzenes do not form salts, it is probable that the salts of metanitrophenol are true phenolates.

66. "*The Maximum Pressure of Naphthalene Vapour*," By R. W. Allen, M.A.

An accurate knowledge of the amount of naphthalene required to saturate a given volume of gas at various temperatures is of great importance to gas engineers. The author has therefore determined the vapour pressure of naphthalene both by the "evaporation" and the "barometric" methods, and obtained results which are in entire accord, but which differ notably, especially at the lower temperatures, from the few measurements given by Naumann. The paper contains tables giving the pressures obtained by both methods as well as one giving the weight of naphthalene required to saturate a cubic metre of gas at temperatures varying from 0° to 130°.

67. "*Scoparin.*" By Arthur George Perkin.

Scoparin, the colouring matter of broom (*Spartium Scoparium, L.*) was discovered by Stenhouse (*Annalen*, 1851, lxxviii., 17), who assigned to it the provisional formula $C_{21}H_{22}O_{10}$ (mean of analyses, C = 57·67; H = 5·34). Hlasiwetz (*Annalen*, 1866, cxxxviii., 190) included scoparin in the quercetin group, for, on fusion with alkali, it gave phloroglucinol and protocatechuic acid.

The similarity of the dyeing properties of scoparin and vitexin pointed to their close relationship (*Trans.*, 1898, lxxiii., 1019. The results of Stenhouse and Hlasiwetz (*loc. cit.*) have been confirmed, as analysis gave C = 57·60, H = 5·09, and fusion with alkali at 220°, phloroglucinol and protocatechuic acid. Digested with hydriodic acid, one molecule of methylic iodide is evolved (found, CH_3 = 3·88), and a new colouring matter, *scoparein*, results, distinguished from scoparin by its strong tinctorial properties. With boiling potassium hydrate solution, scoparin gives phloroglucinol, vanillic acid, and a third substance, $C_9H_{10}O_3$ (found, C = 64·82; H = 6·17) colourless needles m. p. 114°. As this latter contains one methoxy-group (found, CH_3 = 9·65), reacts with semicarbazid, and on fusion with alkali gives protocatechuic acid, it is a *dihydroxyacetophenonemonomethyl ether* (probably OH ; OCH_3 : $COCH_3$ = 1 : 2 : 4).

Solutions of vitexin and scoparin in sulphuric acid, when heated, both develop a dull green colouration. The former, by decomposition with alkali, gives *p*-hydroxy-acetophenone and phloroglucinol, and it is thus very probable that scoparin is a *methoxy-vitexin*. The author intends to investigate this colouring matter further.

68. "*On a new Compound of Arsenic and Tellurium.*" By E. C. Szarvasy, Ph.D., and C. Messinger, Ph.D.

Whilst investigating the compounds which arsenic forms with the elements of the oxygen group, a regularity in their properties was observed, which led to the discovery of a new telluride. The investigation aimed chiefly at a study of the behaviour of these compounds at high temperatures, and the determination of their molecular weights by means of their vapour densities.

Selecting from each group of the compounds examined those most stable at high temperatures, a certain numerical regularity was observed between their molecular weights. In the series of compounds having the formulæ As_2O_3, As_2S_2, As_2Se, the differences between the molecular weights of such a series are 16 and 15 units respectively. Similarly, we may determine the formula of the next probable tellurium compound higher in the series, having the same difference between it and the preceding member. Calculation indicated the formula of this compound to be As_8Te_3. It was subsequently prepared by melting its components together in the ratio 8As : 3Te in a sealed tube under pressure. The vapour density of this compound was also determined. The paper concludes with a comparison of the properties of the compounds which arsenic forms with the various elements of the oxygen group.

69. "*The Action of Hydrogen Peroxide on Secondary and Tertiary Aliphatic Amines. Formation of Alkylated Hydroxylamines and Oxamines.*" By Wyndham R. Dunstan and Ernest Goulding.

In a previous communication (*Proc.*, 1899, xv., 58), the authors have shown that methyl iodide reacts with hydroxylamine, forming *trimethylamine oxide* or *trimethyloxamine*, $(CH_3)_3N{:}O$, whilst ethyl iodide forms first *β-diethylhydroxylamine*, $(C_2H_5)_2NOH$, and by further action *triethyloxamine*, $(C_2H_5)_3N{:}O$.

The constitution of these oxamines suggested the possibility of their formation from the corresponding amines by the action of weak oxidising agents. The authors find that trimethylamine is readily oxidised in aqueous solution by standing in the cold with a dilute solution of hydrogen peroxide, forming *trimethyloxamine* identical in properties with the compound already described. Similarly, triethylamine is readily oxidised to *triethyloxamine*. In both cases, the yield is nearly quantitative. Diethylamine, under the same conditions, is converted into *β-diethylhydroxylamine* identical with the compound prepared by the authors by the reaction of ethyl iodide with hydroxylamine. Experiments are now being made with other amines and with ammonia.

70. "*The Enantiomorphously Related Tetrahydroquinaldines.* By William Jackson Pope and Stanley John Peachey.

Dextrotetrahydroquinaldine was obtained by Ladenburg (*Ber.*, 1894, xxvii., 77) by crystallising the externally compensated base with tartaric acid, when dextrotetrahydroquinaldine bitartrate is eventually obtained in a state of purity. Lævotetrahydroquinaldine has not previously been prepared.

On dissolving externally compensated tetrahydroquinaldine in hot water, by addition of a half-molecular proportion each of hydrochloric and dextro-α-bromocamphorsulphonic acids, and allowing to cool, *lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate*,—

$$C_{10}H_{13}N,C_{10}H_{14}BrO{\cdot}SO_3H,$$

separates in almost quantitative yield. The salt is sparingly soluble in water, and is purified by two or three re-crytallisations from alcohol; it crystallises in colourless needles melting at 218—220°, and on treatment with soda the base separates as an oil, which is extracted

with ether and purified by distillation under reduced pressure.

Lævotetrahoydroquinaldine, $\begin{matrix} CH{:}CH{\cdot}C{\cdot}CH_2{\cdot}CH_2 \\ | \quad | \quad | \\ CH{:}CH{\cdot}C.NH.CHMe \end{matrix}$, is a colourless, highly refractive oil, of faint basic odour, and boils at 158° under 59 m.m. pressure. It has a specific gravity of 1·0236 at 14·5°/4°, and gives the rotation $\alpha_D = -58·60°$ in a 100° m.m. tube at 16°; the specific rotation is therefore $[\alpha]_D = -57·25°$. For the relations of the dextro-isomeride, Ladenburg gives $\alpha_D = +58·35°$ and $[\alpha]_D = +55·99°$ having apparently used the density of the externally compensated base in calculating the specific rotation.

Benzoyl-lævotetrahydroquinaldine, $C_{10}H_{12}N{\cdot}COPh$, is readily obtained, by shaking the base with dilute soda and benzoyl chloride, as a granular crystalline mass, which is purified by crystallisation from ethyl acetate. It separates from cold acetone in lustrous colourless monosymmetric prisms melting at 117—118°, and has the specific rotation $[\alpha]_D = +247·3°$ in a 3·5 per cent benzene solution. A comparison of its properties with those of Walter's optically inactive benzoyltetrahydroquinaldine (*Ber.*, 1892, xxv., 1261) shows that the latter is a true racemic compound.

After filtering off the lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate, the mother-liquor is made alkaline, and the crude dextrotetrahydroquinaldine extracted with ether, and converted into dextrocamphorsulphonate by addition of the requisite quantity of Reychler's camphorsulphonic acid (*Bull. Soc. Chim.*, 1898, [iii.], xix., 120); a crystalline substance separates, which, after repeated re-crystallisation from acetone, yields *dextrotetrahydroquinaldine dextrocamphorsulphonate*,—

$$C_{10}H_{13}N,C_{10}H_{15}O{\cdot}SO_3H.$$

This salt crystallises in colourless needles melting at 127—128°, and has the specific rotation $[\alpha]_D = +45°$ in a 4 per cent aqueous solution; it yields Ladenburg's dextrotetrahydroquinaldine when treated with soda. *Lævotetrahydroquinaldine dextrocamphorsulphonate*,—

$$C_{10}H_{13}N,C_{10}H_{15}O{\cdot}SO_3H,$$

also crystallises well, separating from acetone solution in long colourless needles melting at 137—138°; it has the specific rotation of $[\alpha]_D = -16°$.

Benzoyldextrotetrahydroquinaldine, $C_{10}H_{12}N{\cdot}COPh$, is completely analogous to its enantiomorphously related isomeride; it melts at 117—118°, and has the specific rotation of $[\alpha]_D = -247·4°$ in a 4 per cent benzene solution. The benzoyl derivatives now described are hydrolysed by prolonged boiling with hydrochloric acid, yielding benzoic acid and the original base.

PHYSICAL SOCIETY.

Ordinary Meeting, May 12th, 1899.

Professor Perry, Vice-President, in the Chair.

Dr. Lehfeldt read a note on "*The Vapour-pressure of Solutions of Volatile Substances.*"

The change in vapour-pressure of a solvent due to the solution in it of a small quantity of volatile material has been calculated on the basis of Raoult's note for the corresponding case of a non-volatile dissolved body. The author has interpreted the formula of Nernst in the following words:—When a small quantity of volatile substance is dissolved in a liquid, the vapour-pressure of the liquid is altered in the ratio of the molecular fractional amount of solvent in the liquid to that in the vapour. In order to test this formula it has been applied to the results of experiments made on four series of liquids, viz., alcohol with benzene and toluene, and carbon tetrachloride with benzene and toluene. In the case of normal solutions—such as carbon tetrachloride in toluene, carbon tetrachloride in benzene, and benzene in carbon tetrachloride—the agreement between the observed and calculated values of the percentage composition of the liquid was remarkably good. In the case of toluene in carbon tetrachloride the solution contained about 29 per cent of the dissolved body, and, as the range of applicability of the formula had probably been exceeded, the agreement was not so good as in the previous examples. The mixtures containing alcohol show maxima of vapour-pressure, and on this account the departure from the formula is so much more marked that it is impossible to apply it except in the case of very dilute solutions. The temperature used throughout the experiments was 50° C.

The Secretary read a note by Prof. W. B. Morton and Dr. Barton on the discussion of their paper "On the Criterion for an Oscillatory Discharge of a Condenser." In the discussion which followed the reading of the paper it was pointed out that the result obtained, viz., that on taking into account the distribution of the current in the wire, a condenser having the critical capacity on the simple theory gives an oscillatory discharge, seems to be contradicted by the well-known fact that the resistance of the wire is greater and the inductance less for oscillatory than for steady currents. The explanation of the apparent paradox is to be found in the effect of the damping on the inductance. When the damping is great and the frequency small, as in the neighbourhood of the critical case, what may be termed the equivalent inductance becomes greater than the steady current value. It is shown that this increase in "L" outweighs the increase of "R" in its effect upon the criterion for oscillatory discharge. An examination of the expression for the equivalent inductance in the case of iron shows that it is greater than the steady-current value if the ratio of one amplitude to the next is greater than $e^{\frac{n}{200}}$ where n is the frequency of the oscillation. Since the decrease of "L" with maintained oscillations is due to a surface concentration of current, it is suggested that there must be an axial concentration in the case of damped vibrations. Following the method of Maxwell for determining the current density at a distance from the axis of a wire, an expression for the current was introduced containing a damping coefficient. The "quasi-amplitude" of the disturbance at any point in the wire was thus obtained. An examination of the result shows that making the damping zero indicates a surface concentration. If, on the other hand, the damping is great, the expression for the amplitude increases as the distance from the axis decreases, and we get an axial concentration. Assuming sufficient damping to produce this effect, is is shown that as we go through the point—

$$r = \frac{a}{\sqrt{2}},$$

where "a" is the radius of the wire we pass from a greater value of current density in the inner parts to a less in the outer than would correspond to a uniform distribution throughout the wire. From general reasoning the authors think that if a rapidly damped disturbance is propagated into a wire from its boundary, and if the oscillations are slow enough to allow the current to penetrate to the core, we should expect to find an axial concentration in the latter stages of the phenomenon.

Dr. Lehfeldt said that Prof. Lodge had pointed out, at the reading of the paper, that the solution the authors obtained changed character at the critical resistance. As this point had not been considered in the note, he supposed that the change in character made no difference to the results obtained.

The Chairman expressed his interest in the proof of the existence of an axial concentration.

Mr. Addenbrooke exhibited and described a quadrant electrometer for application to alternating current measurements. The author has substituted for cylindrical quadrants two sets of flat plates, the top set being adjust-

able. In this way the range of the instrument is considerably increased. The ability to remove one or more of the top quadrants makes the needle very accessible. By lowering the needle on to the bottom quadrants, and then bringing down one of the top plates, the instrument can be carried with safety. One of the top quadrants can be worked up and down with a worm gear, and by this motion the "electrical zero" of the electrometer is obtained. The suspension consists of a flat phosphor bronze strip, the torsion of which is found to be perfectly uniform, there being no fatigue effect. The case of the instrument contains windows, so that the needle can be viewed from two directions at right angles, and there are screw motions to centre the needle with respect to the quadrants. To reduce the effect of air convection currents upon the needle, the inside of the case is lined with cotton velvet. The quadrants are supported on brass bars passing through long ebonite sleeves in the bottom of the instrument. This gives good insulation without the use of sulphuric acid, and there is no Leyden jar or condenser in connection with the needle. Whan using the electrometer idiostatically, with the finest strip, a light needle, and the quadrants one-tenth of an inch apart, a difference of potential of 1 volt will produce a deflection of about 5 m.m. upon a screen 2 metres distant. Using the instrument heterostatically, with 100 volts on the needle, one-fifth of an inch between the quadrants and half a volt acting across them, a deflection of 200 m.m. can be obtained. This sensitiveness is about twelve times as great as that got from instruments designed by Kelvin, Mascart, and Haga. Mr. Addenbrooke then showed how, in conjunction with a voltmeter and an ammeter, it was possible with his instrument to determine sll the factors of an alternating current system. One increased sensitiveness of the electrometer renders it possible to measure currents of any magnitude with a very small waste of energy.

Mr. Gaster pointed out that the measurement of self-induction with an electrometer could only be carried out practically if the current curve was a sine curve. He said that in curves obtained from a Ganz motor a correction amounting to 7 per cent had to be applied.

The Chairman said that even if the curve obtained was a sine curve, the electrometer was never used in this country for measuring self-induction.

Prof. Herschell asked if it were possible to adjust the quadrants after the needle had been charged.

Mr. Addenbrooke then purposely disturbed the position of the adjustable plate, and, after charging the needle, reduced the deflection to zero by the worm gear. The author said that for high voltages the curve of calibration was different to that obtained from the ordinary formula.

The Chairman said that this discrepancy was probably due to want of perfect symmetry. In a paper read before the Royal Society, by Perry, Ayrton, and Mather, it was shown that the presence of the guard around the mirror of an ordinary electrometer was sufficient to affect the needle when working with high voltages. In working with the plates very close together, he was afraid the symmetry would be liable to be disturbed by a slight tilting of the needle due to electrostatic attraction.

The author observed that the plates were only very close together when working with low voltages.

The Vice-President proposed votes of thanks, and the meeting adjourned until May 26th.

CORRESPONDENCE.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

Sir,—The letters by Mr. Pattinson and Prof. Lunge referring to my letter in the Chemical News of March 30th (vol. lxxix., p. 155) have been read by me with great interest.

I regret Prof. Lunge considers it necessary to include my method of calculation amongst the erroneous methods —which he assumes I have not observed—quoted on page 106, vol. ii., of his book. The reason I expressed my astonishment at Prof. Lunge in my letter was based principally on the perusal of the above-mentioned page of his magnificent work.

I must apologise to Prof. Lunge, and also Mr. Pattinson, for having attributed the compilation of the table under dispute to the wrong person.

I regret I cannot agree with Mr. Pattinson's argument referring to his table and the "Tyne" test.

To my mind it resolves itself into a matter of how the standard acid is prepared, and the old-established law of equivalents.

With regard to the preparation of the standard acid, we find the following statement in Lunge (vol. ii., p. 106):—

"On the Tyne the equivalent of sodium carbonate was taken at 54 instead of 53, and the test-acid made so that a litre of it saturates 54 grms. pure Na_2CO_3."

Mr. Pattinson states in his letter that the test-acid on the 32 equivalent is weaker than the true normal acid!

Let us assume that Prof. Lunge's description of preparing the test-acid is the basis of the method generally adopted—which it must be, unless somebody is making an awful mistake—and apply the principle of equivalents to it. Thus, a normal acid which saturates 54 parts Na_2CO_3 will neutralise 41 parts NaHO or 32 parts Na_2O, which means that a sample of pure caustic soda tested with this acid would yield 78·05 per cent Na_2O. Take a simple example to illustrate:—Weigh out 4·1 grms. NaHO, and assume it required 100 c.c. test-acid to neutralise it; then the sample would contain—

$$\frac{100\times4\cdot1}{4\cdot1}=100 \text{ per cent NaHO or } \frac{100\times3\cdot2}{4\cdot1}=78\cdot05 \text{ per cent } Na_2O.$$

Am I not, therefore, justified in saying that Mr. Pattinson's table is wrong, as far as caustic soda is concerned?

With regard to the abolition of the 32 equivalent, is it not a matter for the consumers to take up? The manufacturers can hardly be expected to take action on their own account.—I am, &c.,

H. A. Hooper.

Chicago, Ill., U.S.A., May 1, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES

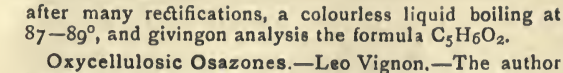
Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 17, April 24, 1899.

Furfuric Alcohol.—G. André.—Furfuric alcohol, $C_5H_6O_2$, is a substance about which little is known. It is difficult to prepare in large quantities and spontaneously alters after a few hours. The author has repeated Hugo Schiff's preparation with many refinements, to obtain the substance in a state pure enough for determining its heat of formation, to complete the series of thermal relations recently found by MM. Berthelot and Rivals. Furfurol is placed in contact with very slight excess of concentrated aqueous potash solution. The mixture becomes heated and turns into a reddish mass. The furfuric alcohol dissolves in water together with pyromucate of potassium and the unattacked furfurol. This aqueous solution is saturated with CO_2, and then the alcohol extracted with ether. The author obtained by this method,

after many rectifications, a colourless liquid boiling at 87—89°, and givingon analysis the formula $C_5H_6O_2$.

Oxycellulosic Osazones.—Leo Vignon.—The author has previously shown that cotton absorbs phenylhydrazine. He now publishes his researches on the precise reaction which takes place when phenylhydrazine acts on the cellulose of cotton and some of the derivatives of oxidation. The formation of osazones from oxycelluloses corroborates the hypothesis that has already been stated about the oxycellulosic molecule. The osazone group of the oxycelluloses would be—



Journal de Pharmacie et de Chimie, Series 6, Vol. ix., No. 1.

The Transformation of the Carbonate of Orthocresol into a Homologue of Orthocresol Phthalein.—P. Cazeneuve.—Already inserted.

No. 2.

The Action of B. Coli and of Eberth's Bacillus on the Nitrates.—L. Grimbert.—This has already been inserted in full.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Royal Institution, 5. Adjourned General Meeting.

TUESDAY, 23rd.—Royal Institution, 3. "Recent Advances in Geology," by Prof. W. J. Sollas, D.Sc., F.R.S.

THURSDAY, 25th.—Royal Institution, 3. "Water Weeds," by L. C. Miall, F.R.S.

FRIDAY, 26th.—Physical, 5. "On the Thermal Properties of Normal Pentane" (Part 2), by Prof. S. Young and Mr. Rose-Innes. "On the Distribution of Magnetic Induction in a Long Iron Bar," by C. G. Lamb.

—— Royal Institution, 9. "Climbs and Explorations in the Andes," by Sir William Martin Conway, M.A.

SATURDAY, 27th.—Royal Institution, 3. "The Music of India and the East, and its Influence on the Music of Europe" (with Musical Illustrations), by Edgar F. Jacques.

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THE CHEMICAL NEWS.

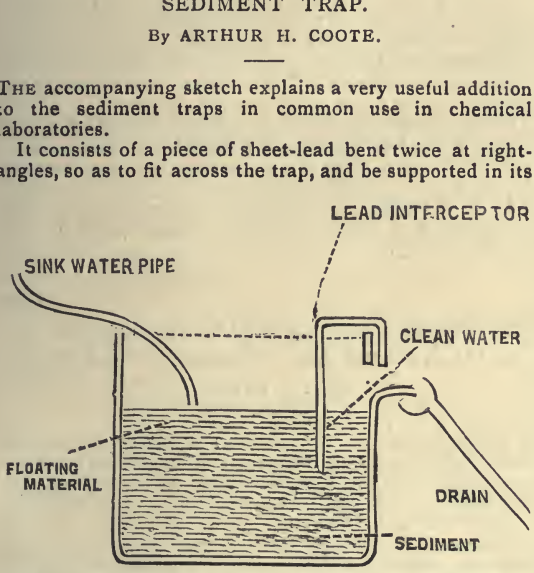
Vol. LXXIX., No. 2061.

SEDIMENT TRAP.

By ARTHUR H. COOTE.

The accompanying sketch explains a very useful addition to the sediment traps in common use in chemical laboratories.

It consists of a piece of sheet-lead bent twice at right-angles, so as to fit across the trap, and be supported in its



place by the front and sides of the trap. It effectually prevents paper, matches, corks, &c., either from choking the outlet and causing the trap to overflow or from passing into the drain itself.

A plumber can fit any number of such in a very little time.

Ordnance College, Woolwich,
May 9, 1899.

A NEW METHOD FOR THE ESTIMATION OF CARBONIC OXIDE.

By MM. SCHLAGDENHAUFFEN and PAGEL.

M. Nicloux has recently published a method for the estimation of carbonic oxide, based on the oxidation of this gas on contact with anhydrous iodic acid at a temperature of 150°, according to the following reaction:— $5CO+2IO_3H=5CO_2+H_2O+I_2$.

The apparatus of which he makes use is arranged so as to absorb the iodine by means of a weak solution of caustic soda. When the operation is ended we add a little nitrite of soda and sulphuric acid until the reaction is distinctly acid; agitate with sulphide of carbon, and titrate the more or less coloured solution by comparison with a typical solution containing a known quantity of iodine.

On examining the very simple equation of this reaction it seemed probable to us that other oxygenated compounds might behave in a similar manner. We therefore undertook a first series of experiments with molybdic, chromic, arsenic and arsenious, stannic, antimonic and antimonious acids, but without the slightest success, since none of them was reduced either at 150° or at higher temperatures varying between 200° and 300°.

Following up these negative results, we commenced a new series of operations with some metallic oxides,—oxides of silver, lead, bismuth, and copper,—with the following results:—

1. *Oxide of Silver.*—Oxide of silver, previously dried in an air-oven at a temperature of 150° and placed in a U-tube in a water-bath, is submitted to the action of a current of pure carbonic oxide, absolutely free from carbonic acid, by means of a flask filled with baric hydrate. On leaving the experimental tube the gaseous current passed through another barytic solution which begins to become cloudy when the temperature reaches 50°. Between 54° and 60° the white precipitate becomes very abundant, and thus indicates the presence of a large proportion of carbonic acid. At the same time the colour of the oxide of silver changes; the original dark brown colour gives place to a brilliant white appearance. By gently shaking the U tube, so as to allow the gas to penetrate the pulverulent material more intimately, we find that the operation is terminated after the lapse of a few minutes. The deoxidation of the metallic oxide is thus effected, and the carbonic oxide is transformed into carbonic acid.

To decide whether it is possible to formulate this experiment thus, $CO+Ag_2O=CO_2+Ag_2$, we substituted for the barytic solution a Liebig's tube filled with potash at 50 per cent, weighed before and after the passage of the gas. With 2 grms. of oxide of silver we observed, under the same conditions as to temperature as above, a loss of 0·145 grm. of oxygen. The corresponding quantity of carbonic acid is by calculation 0·385 grm: this figure is absolutely the same as that given by the increase of weight of the potash tube, which, therefore, proves that the experiment is entirely in accord with theory, and that the above formula is justified.

2. *Cuprous Oxide.*—We take cuprous oxide, heated in the air-oven to 150°, and proceed as above, placing the U-tube in a water-bath, but nothing comes over even when the water is boiled; the barytic solution does not become cloudy. By using an oil-bath we notice a slight cloudiness at about 125°. The precipitate of carbonate of baryta becomes abundant at 215°; at this moment the colour of the material in the tube changes, becoming red, instead of brown as it was originally. Then, towards 300°, we notice a lively incandescence take place, indicating the end of the operation, and the whole of the oxide is transformed into metallic copper, having a crystalline aspect. The reaction is effected in the same manner as the preceding one, viz., $CO+Cu_2O=CO_2+Cu_2$, from which we may safely say that it is the result of an estimation carried out under the same conditions as those with the oxide of silver. We have in fact:—

Oxygen used	2 grms.
Loss of oxygen	0·25 grm.
Theoretical amount of carbonic acid..	0·680 ,,
Carbonic acid found	0·685 ,,

The concordance between the two latter figures is perfect, since the temperature to which we carried the cuprous oxide was a little too high. At 150° the suboxide begins to change into cupric oxide; this is a source of error easy to prevent.

3. *Oxide of Bismuth.*—In submitting oxide of bismuth, dried at 150°, to the action of a current of carbonic oxide, on an oil-bath at 230°, the barytic solution through which the gas passes commences to become cloudy. The precipitate increases at 260°, at the same time as the colour of the material changes; it becomes yellow, instead of white as it was originally. Between 385° and 400° it becomes black, and changes into the suboxide, but not into metallic bismuth. This result might, however, be foreseen, as various writers agree that the suboxide is very difficult to reduce. If, instead of allowing the suboxide to cool in the experimental tube, we throw it out while still warm, it changes rapidly into Bi_2O_3 with bright incandescence.

4. *Oxides of Lead.*—The oxidised compounds of lead behave in different manners on contact with carbonic oxide. With minium, for example, we notice that deoxidation already begins at 225°, while litharge does not appear to be attacked below 300°. The white oxide, derived from the hydrate, previously heated in the oven to 150°, is deoxidised with still greater difficulty. It gives metallic lead when the temperature of the oil-bath is carried to 430°, but the reaction is not so sharp as with the oxides of silver and copper, since the metal remains mixed with a certain quantity of suboxide, without, however, containing carbon, as stated by M. Boudouard in speaking of Lowthian Bell's experiments.

To sum up, the oxides of silver and copper, heated in a current of carbonic oxide, are entirely deoxidised, the first at 60°, the second at 300°, and may consequently serve to completely absorb this gas. As the carbonic acid formed corresponds theoretically with the oxygen lost, it follows that this reaction constitutes a new method for the estimation of carbonic oxide.—*Journ. de Pharm. et de Chim.*, Series 6, vol. ix,, No. 4.

ACTION OF THE METALLIC SULPHATES ON PARATUNGSTATE OF POTASSIUM.

By L. A. HALLOPEAU.

In a research on the acid tungstates, von Knorre described several double paratungstates, obtained by the reaction in the wet way, of some metallic sulphates on paratungstate of sodium.

I have found that the metallic sulphates react on paratungstate of potassium in an analogous manner; but the study of the products of the reaction is much more difficult than in the case of the sodium salt, on account of the paratungstate of potassium being less soluble. I was, however, enabled to distinctly obtain the following double paratungstates by this method:—

Paratungstate of Potassium and Magnesium.—This compound is prepared by mixing two solutions containing equal molecular weights of paratungstate of potassium and sulphate of magnesium. On concentration the double salt is deposited. It is almost completely insoluble in cold water, but can be dissolved in warm water, which enables us to purify it by a fresh crystallisation. The product thus obtained answers to the formula $12WO_35(2/3K_2O+1/3MgO)+24H_2O$.

	Found. I.	Found. II.	Calculated.
$12WO_3$	77·28	76·86	77·42
$10/3K2O$	9·04	8·92	8·71
$5/3MgO$	2·09	2·41	1·86
$24H_2O$	11·60	11·89	12·01
	100·01	100·08	100·00

These crystals have, under the microscope, the appearance of prisms, sometimes taking the form of hexagonal tablets; they act strongly on polarised light, showing extinctions parallel to the direction of the axes. They lose 17 molecules of water at 100°, that is to say, 8·40 per cent—theory requires a loss of 8·50 per cent.

Paratungstate of Potassium and Manganese. — By mixing two solutions, containing equal molecular weights of paratungstate of potassium and sulphate of manganese, we instantly obtain a yellowish-white precipitate in the form of microscopic crystals, completely insoluble in water. After prolonged washing with warm water, this salt answers to the formula $12WO_3,3K_2O,2MnO+16H_2O$. These crystals are colourless, rhomboidal prisms, with modified angles, very refrangible, and acting strongly on polarised light. They lose 10 molecules of water at 100°, that is to say, 5·21 per cent—theory requires 5·15 p. c.

	Found. I.	Found. II.	Found. III.	Calculated.
$12WO_3$	79·58	79·72	80·09	79·63
$3K2O$	7·79	—	—	8·07
$2MnO$	4·74	4·40	—	4·06
$16H_2$	8·05	8·10	—	8 24
	100·16			100·00

There is also formed a compound, slightly soluble in water, when we pour a solution of sulphate of zinc into a solution of paratungstate of potassium; but the crystals of this salt are always accompanied by crystals of paratungstate of potassium, which separate out at the same time.

By the action of sulphate of calcium on paratungstate of potassium, we obtain an amorphous insoluble precipitate. The same thing occurs with most other metallic sulphates; but these insoluble double salts are often mixed with tungstic acid, especially when the solution of the sulphate is acid.—*Bull. Soc. Chim.*, Series 3, vol. x·x.-xx., No. 23.

ON AQUEOUS SOLUTIONS OF METALLIC GOLD, AND ON THE PURPLE OF CASSIUS.

By C. L. REESE.

In a recent number of the *Annalen de Chemie* (ccci., 29), Richard Zsigmondy has published an interesting account of soluble metallic gold, obtained by reducing gold chloride in very dilute aqueous solution. The following is an abstract of his paper:—

Gold can be held in solution in water in different coloured conditions. Although the great variety of colours obtained from the colloidal silver of M. Carey Lea cannot be obtained with gold, yet gold solutions are obtained which are deep-red, blue, and black, as well as of shades lying between these colours, according to the conditions under which the gold is reduced. The blue or violet solutions seem to be the most easily obtained. The red gold solution is the one principally studied. It is obtained by treating very dilute, boiling hot, and slightly alkaline solutions of gold chloride with different reducing agents, such as formic aldehyde, acetic aldehyde, alcohol, or even hydroxylamine. Many attempts were made, with varying success, but the best conditions are the following: 25 c.c. of a solution of chlorauric acid, $AuCl_3$·HCl containing 0·6 grm. to the litre, diluted with 100 to 150 c.c. of pure distilled water, and rendered alkaline by the addition of 2 to 4 c.c. of a $\frac{n}{10}$ normal solution of potassium carbonate, are heated to boiling. As soon as the liquid begins to boil, it is removed from the flame, and 4 c.c. of a solution of 1 part of freshly distilled formic aldehyde in 100 parts of water is added gradually to the boiling-hot gold solution. In a short time the colourless liquid darkens, becomes light red, and in a few seconds attains a deep-red colour, which does not change in the slightest degree on boiling or on standing for months.

If the above directions are not strictly adhered to, not clear red, but darker purple and often violet and blue-black, turbid liquids are formed. The very dilute red solution can be evaporated to half its volume without change, but further boiling will cause it to change to a dark-violet colour, and gold will be precipitated as a black powder. The precipitation is probably due to the accumulation of salts which tend to precipitate the dissolved colloidal gold. The solution was purified by dialysis at a temperature of 40° to 50°. The solution can thus be reduced to one-twentieth of its volume in a few days, and solutions containing 0·12 per cent colloidal gold were obtained, but on further concentration metallic gold was precipitated on the parchment.

The red gold solution passes through the closest filter-paper without change. It is tasteless. On addition of neutral salts, acids, or fixed alkalis, the beautiful red colour changes to blue; the liquid becomes turbid, gradually losing its colour, and in eight or nine hours the gold all falls to the bottom as a blue-black powder. Potassium ferrocyanide seems to act differently from other salts; it changes the colour to green, and after twenty-eight hours to pure yellow, but the gold is not precipitated. Ammonia changes neither the colour nor the solubility of the gold. The addition of an excess of alcohol changes the colour to dark-violet and precipitates the gold completely, but the precipitate, at times, retains its solubility in water.

The metallic gold in aqueous solution acts just as most other dissolved colloidal substances when subjected to electrolysis, following the negative electricity to the positive pole, where it is deposited as a black powder, which can readily be recognised as metallic gold when allowed to dry, as it immediately assumes a beautiful gold lustre. When a membrane is placed between the electrodes, the gold, like a true colloid, does not pass through the membrane, but is deposited upon it on the negative side.

Mercury does not amalgamate with dissolved gold either on being agitated with the solution or on boiling, and even when precipitated with salts amalgamation takes place very slowly and incompletely.

That the dissolved body is really metallic gold and not aurous oxide is shown by analysis of the precipitate caused by sodium chloride. The very small volume of oxygen found is undoubtedly due to air condensed on the surface of the very finely divided precipitate while drying, especially as the equivalent volume of nitrogen was also found.

When we consider the results of analysis, together with the fact that gold with metallic lustre is deposited on slow evaporation, and further that the reduction was carried out in a boiling-hot solution, and by means of a strong reducing agent, there can be no doubt that the red solution contains gold in the metallic condition.

The similarity between the colours of these solutions of gold and the colours of thin layers of gold by transmitted light is marked as well as that of red and rose ruby glass. The absorption spectra of the red solution compared with ruby glass, of the blue and violet solution with blue and violet colours of thin layers of metallic gold by transmitted light, are almost identical.

In an appendix to his paper the author referred to the fact that Faraday, in a paper on the "Experimental Relation of Gold to Light" (*Phil. Trans.*, 1857, p. 145), described many of these phenomena, and actually obtained the red solution of gold, but did not recognise it as such, attributing the colour to suspended gold in a finely divided condition.

In the same number of the *Annalen* (*Ann. Chem.*, Liebig, cccl., 361), Zsigmondy has published another article on "The Chemical Nature of the Purple of Cassius," in which the nature of this curious substance seems finally to be cleared up.

There are few substances in the field of inorganic chemistry on which so much has been done and so much written with as little result as this purple of Cassius. Up to the present time there have been two views held as to the chemical nature of this substance:—the one, that it is a mixture of stannic acid and metallic gold; and the other, that of Berzelius, that it is substantially a chemical compound of purple gold oxide with the oxides of tin, possibly mixed with an excess of stannic acid.

The solubility of the substance in ammonia favours the latter view, although Schneider lays great stress on its colloidal character, and considers the ammoniacal solution as a mixture of the "hydrosols" of gold and stannic acid.

It seemed very likely that the substance is a chemical compound of acid character, and that the solubility in ammonia is due to the formation of a salt, but it was found that by oxidation of stannous chloride, and by allowing very dilute solutions of stannic chloride to stand, the "hydrogel" of stannic acid separated out, which on the addition of a few drops of ammonia liquefied, and so became soluble in water, just as the purple of Cassius does. There can therefore be no salt formation here.

After the solutions of metallic gold in water were obtained, a substance in every way identical with the purple of Cassius was made by mixing colloidal stannic acid with colloidal gold, and precipitating with acids.

The paper is divided into three parts, the first of which is devoted to showing that the substance is not of acid character in its relation to ammonia, and to the preparation of colloidal stannic acids. This part of the work was done with J. Robitschek.

The purple of Cassius was prepared according to the method of Golfier Besseyre (*Ann. Chim. Phys.*, liv., 40), from stannous chloride solution, free from stannic chloride, and gold chloride. The washed and dried preparation was soluble neither in ammonia nor in caustic potash, but when moistened with hydrochloric acid it was easily soluble in water. When fresh and moist it is insoluble in concentrated ammonia, potassium hydroxide, or potassium carbonate, but dissolves on dilution. The ammonia solution can be boiled if left dilute so that no odour of ammonia can be detected even on addition of caustic potash, and only a trace can be detected by titration, without precipitating the substance. That the solubility in ammonia or potassium hydroxide is not due to the formation of a salt is also shown by the small percentage of these substances found on analysis—0·003 ammonia in 1 grm. and 0·4 c.c. normal alkali in 1 grm. The solubility in these reagents seems to be due to the liquefying property of the alkalis. The purple of Cassius behaves in every way like a colloid substance toward the electric current and porous membranes.

By passing a strong current of air through a very dilute solution of stannous chloride, free from gold, and allowing it to stand, it was oxidised gradually to a colloid stannic acid, which is precipitated, and, when washed free from chlorine, behaves toward reagents neither like ortho- nor meta-stannic acid. It is insoluble in strong hydrochloric acid, nitric acid, or caustic potash, but dissolves immediately on diluting to double the volume. It is soluble in water after moistening with ammonia. We have here the "hydrogel" of stannic acid which behaves toward the electric current like the purple of Cassius.

A colloidal stannic acid can also be obtained from stannic chloride when a very dilute solution of the latter (2 grms. in 3 litres) is allowed to stand for several hours. A voluminous precipitate comes down, which, when washed free from chlorine, moistened with a few drops of ammonia, and diluted, dissolves to a clear liquid which can be boiled without precipitation of stannic acid. This preparation differs from the former in that it is soluble in strong or dilute hydrochloric acid and potassium hydroxide, and not entirely in nitric acid. Potassium carbonate precipitates it from its hydrochloric acid solution, but does not dissolve it in excess.

From their properties these forms of stannic acid are seen to be neither ortho- nor meta-stannic acid; but they can be looked upon as colloidal mixtures of the two rather than individuals lying between the two, the properties of the one being hidden by those of the other. The purple of Cassius is such a mixture of gold and stannic acid hydrate, in which the stannic acid imparts to the metallic gold the property of dissolving in water by means of alkalis. This is the reason why so many chemists have for so long a time considered the substance to be a chemical compound. By mixing a solution of either of these colloidal stannic acids with a solution of colloidal gold, and precipitating by means of dilute acids or salt solutions, a gold-purple can be obtained of any

desired composition and intensity of colour—in fact, any of a great variety of shades. The mixture does not turn blue, and then precipitate gold when treated with acids or salts, like the red gold solution, but remains unchanged even on long standing; but when boiled a red body is precipitated, which behaves, in every respect, like the purple of Cassius.

The formation of the purple of Cassius is explained by assuming that when stannous chloride is added to a sufficiently dilute solution of gold chloride, the latter is immediately reduced to metallic gold, while stannic chloride is formed. Generally after a few seconds the liquid becomes red, but the purple is not precipitated for several days unless it is heated. The gold is not precipitated as a black powder, because the stannic chloride formed is immediately hydrolysed into hydrochloric acid and the hydrate of stannic acid. The latter prevents the aggregation of the gold particles, and the stannic acid remains in solution as a colloid, which, on standing, gradually changes under the influence of the dilute hydrochloric acid to an insoluble form, the "hydrogel" of stannic acid. By heating, this change takes place immediately.

The properties of purple of Cassius depend on the properties and character of the stannic acid present, the gold playing a passive *rôle* in its relation to reagents. If the stannic acid is soluble in concentrated hydrochloric acid, so is the purple, but if it has the properties of meta-stannic acid it is insoluble in that reagent, but dissolves on distillation. In the same way the solubility in ammonia or dilute alkalis depends upon the character of the stannic acid present; in fact, the great variety in the properties of the stannic acids explains the many contradictions in the literature with reference to the properties of the purple of Cassius. Zsigmondy says, "I look upon the knowledge that a mixture of colloid bodies can behave under some conditions as a chemical compound, and that the properties of one body in such mixtures can be hidden by those in another, as the most important conclusion to be drawn from this work."

By mixing the "hydrogels" of stannic acid and silver, and precipitating with dilute sulphuric acid, a red-yellow body was obtained, which is soluble in ammonia, and a similar body was also obtained by reducing silver nitrate in the presence of a stannic acid solution.—*Amer. Chem. Journ.*, xxi., No. 2, Feb., 1899.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month of April has been slightly in excess of the thirty years average. The actual fall was 1·83 inches; the average is 1·66 inches, giving an excess of 0·17 inch, and reducing the deficiency for the first four months of the year to 0·23 inch, or 3·1 per cent.

Our bacteriological examinations of 236 samples have given the results recorded in the following table; we have also examined 36 other samples, from special wells, standpipes, &c., making a total of 272 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 23 samples) ..	908
New River, filtered (mean of 23 samples) ..	8
Thames, unfiltered (mean of 24 samples) ..	10622
Thames water, from the clear water wells of five Thames-derived supplies (mean of 120 samples)	22
Ditto ditto .. .. highest	185
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 23 samples) ..	2490
River Lea, from the East London Company's clear water well (mean of 25 samples) . ..	5

Since the beginning of the year the organic carbon in the water has been gradually diminishing, as will be seen by the following table. In spite of the excess of rain, the water during the month of April has had less soluble organic matter in solution, less colour, and its bacteriological quality has gradually improved; although at no time during the year has there been any deficiency in the effective removal of microbes by filtration.

Averages of Five Supplies derived from the River Thames.

	Common Salt. Per gall.	Hardness.	Oxygen reqd. Per gall.	Organic Carbon. Per gall.	Organic Carbon. Per gall.	Colour.
	Means.	Degrees. Means.	Means.	Means.	Max.	Br'n: Blue. Means.
Jan. ..	2·236	15·73	0·072	0·227	0·282	25·4 : 20
Feb. ..	2·144	15·75	0·073	0·207	0·272	26·6 : 20
March .	2·092	16·14	0·037	0·134	0·226	12·5 : 20
April ..	2·147	14·43	0·031	0·093	0·163	8·8 : 20

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE CONSTITUTION OF THE AMMONIUM-MAGNESIUM PHOSPHATE OF ANALYSIS.*

By F. A. GOOCH and MARTHA AUSTIN.

(Continued from p. 233).

IN Table III. are given the results obtained in a study of the effects of varying proportions of ammonium chloride and the soluble phosphate upon the constitution of the precipitate. All precipitates were gathered upon asbestos in the filtering crucible, washed in faintly ammoniacal water, and ignited as usual. In every case the precipitation was practically complete; for, upon allowing the filtrates with the wash-water to stand for several days after further addition of microcosmic salt, nothing but insignificant traces of a precipitate—not exceeding 0·0001

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Series 4, vol. vii., No. 39, March, 1899.

Table III.

	$Mg_2P_2O_7$ corresponding to $Mg(NO_3)_2$ taken. Grm.	$Mg_2P_2O_7$ found. Grm.	Error in terms of $Mg_2P_2O_7$. Grm.	Error in terms of MgO. Grm.	NH_4Cl present. Grm.	$HNaNH_4PO_4.4H_2O$ used. Grm.	Volume. C.m.s
			A.				
1.	0·5311	0·5418	+0·0107	+0·0038	—	2·5	150
2.	0·5311	0·5462	+0·0151	+0·0057	2	2·5	150
3.	0·5311	0·5408	+0·0097	+0·0035	2	2·5	150
4.	0·5311	0·5500	+0·0189	+0·0068	60	2·5	250
5.	0·5311	0·5520	+0·0209	+0·0075	60	2·5	250
6.	0·5311	0·5345	+0·0034	+0·0012	*	2·5	150
7.	0·5311	0·5371	+0·0060	+0·0022	*	2·5	150
8.	0·5311	0·5384	+0·0073	+0·0026	*	2·5	150
9.	0·5311	0·5386	+0·0075	+0·0027	*	2·5	150
10.	0·5311	0·5415	+0·0104	+0·0037	*	2·5	150
			B.				
11.	0·5311	0·5312	+0·0001	+0·0000	*—	2·5	150,100
12.	0·5311	0·5311	−0·0000	+0·0000	*—	2·5	150,100
13.	0·5311	0·5346	+0·0035	+0·0013	2+2	2·5	150,100
14.	0·5311	0·5348	+0·0037	+0·0014	2+2	2·5	150,100
15.	0·5311	0·5383	+0·0072	+0·0026	5+5	2·5	150,100
16.	0·5311	0·5368	+0·0057	+0·0021	5+5	2·5	150,100
17.	0·5311	0·5376	+0·0065	+0·0023	10+10	2·5	200,100
18.	0·5311	0·5395	+0·0084	+0·0030	10+10	2·5	200,100
19.	0·5311	0·5396	+0·0085	+0·0031	60+5	2·5	250,100
20.	0·5311	0·5389	+0·0078	+0·0028	60+5	2·5	250,100

Table IV.

1.	0·5311	0·5503	+0·0192	+0·0069	10	2·5	200
2.	0·5311	0·5505	+0·0194	+0·0070	10	2·5	200
3.	0·5311	0·5393	+0·0082	+0·0029	10, —	2·5	200,100
4.	0·5311	0·5351	+0·0040	+0·0017	10, —	2·5	200,100

grm.—ever appeared. In the experiments of Section A precipitations were made in the cold by the action of microcosmic salt in considerable excess upon the solutions of magnesium nitrate containing varying amounts of ammonium chloride. In Experiments 1 to 5 the liquid was made faintly ammoniacal after the addition of the precipitant, and the precipitate was filtered off immediately after complete subsidence; in Experiments 6 to 10 the precipitate first thrown down was re-dissolved in a very little hydrochloric acid and re-precipitated by dilute ammonia (the operation being repeated several times) with a view to improving the crystalline condition of the precipitate, and this treatment introduced, of course, a small amount of ammonium chloride, probably less than a grm. It will be observed that errors of excess appear in all these determinations, those being the greatest in the experiments in which the largest amounts of the ammonium salt were present.

In the experiments of Section B the manipulation was so changed that the supernatant liquid was poured off (through the filtering crucible which was to be used subsequently to collect the phosphate) after the precipitate had subsided and the insoluble phosphate was dissolved in hydrochloric acid and brought down again, after dilution, by the addition of a faint excess of dilute ammonia. By thus removing the supernatant liquid after the first precipitation, the excess of the precipitant and the amounts of ammonium chloride originally present were reduced to relatively low limits, so that their effects in the re-precipitation were at a minimum; and by adding varying amounts of ammonium chloride, or none at all, before the re-precipitation, it became possible to demonstrate the individual effect of that reagent apart from that of an excess of the microcosmic salt. It will be noted that in Experiments 11 and 12, in which no ammonium salt was added after the decantation from the first precipitate, the results are ideal, and that the errors of excess advance as the amounts of ammonium salt present in the final precipitation increase. The quantity of the ammonium salt present during the first precipitation does not influence the error in the final precipitation unless it is so large that a simple decantation of the supernatant liquid would naturally leave an appreciable amount of it to act when the second precipitation takes place.

It is plain that the errors of excess which appear when either the ammonium chloride or the soluble phosphate is present in considerable amount must be due either to mechanical inclusion on the part of the highly crystalline precipitate or to variation in the ammonium-magnesium phosphate from the ideal constitution toward a condition represented by a phosphate richer in ammonia and correspondingly deficient in magnesium. If any appreciable amount of the ammonium chloride present were held by the precipitate, it would naturally be represented by magnesium chloride after ignition, but, in no one of these experiments—even in those dealing with 60 grms. of ammonium chloride—did the residue, after dissolving in nitric acid, give with silver nitrate evidence of the presence of more than a mere unweighable trace of chloride. A special experiment, moreover, in which an attempt was made to determine the silver chloride precipitated from the solution in nitric acid of an unignited precipitate thrown down by microcosmic salt in presence of 60 grms. of ammonium chloride, confirms this conclusion; the precipitate was unweighable. If ammonium chloride present in the solution to so great an amount is not included in the precipitate in significant quantity, it would seem to be unnatural that the microcosmic salt should be included mechanically in any very great amount. But unless the microcosmic salt was mechanically included, the increase in weight must be due to the chemical influence of the reagents—that is, to the production of a phos-

phate rich in ammonium and deficient in magnesium. Berzelius (*Jahresbericht*, 3 Jahrgang, 1824, übersetzt von C. G. Gmelin, s. 92) recognised the existence of such a phosphate of magnesium; but Wach ("Schweigger," 1830, Band 29, s. 265), in following the work of Berzelius, failed to find it. No attention seems to have been given since to the existence of such a salt. It would be natural to expect its formation, if ever, when the precipitating phosphate is in excess, and ammonium salts are present in abundance, with free ammonia. Obviously the natural effects of all these reagents would be toward the production of a salt holding more ammonia and more phosphoric pentoxide for a given amount of magnesium. The results of the table seem to point strongly to such tendencies, and, by inference, towards the existence of such a compound. Thus, in Experiments 11 and 12, in which the greater part of this excess of microcosmic salt was removed by decantation before the second precipitation, while no ammonium chloride was present excepting the small amount made by the solution and re-precipitation of the first precipitate, the error is practically nothing. In Experiments 13 and 14, 15 and 16, 17 and 18, all similar to 11 and 12, excepting that ammonium chloride was present, the average errors (+0·0036 grm. in terms of magnesium phosphate, 0·0064 grm., +0·0074 respectively) increase as the ammonium chloride is increased in the final precipitation. In Experiments 19 and 20, in which the ammonium chloride amounted to 60 grms. in the first precipitation and to 5 grms. in the second, in addition to the amount that would naturally remain after decanting the strong solution of the former precipitation, the similarity of this error (+0·0082 in the mean) to that of the experiments in which smaller amounts of the ammonium chloride were used throughout goes to show that only the amount of ammonium salt present in the final precipitation counts. Further, a comparison of corresponding experiments of A and B shows very plainly that the treatment which involves the removal of the large part of the microcosmic salt, the solution of the precipitate, and re-precipitation tends to reduce the higher indications. Thus, for example, the error in 2 and 3 is +0·0124 grm. in terms of magnesium pyrophosphate, while in 13 and 14—similarly carried out, except the decantation of the excess of the precipitant, solution, and re-precipitation—the error is +0·0036 grm.

The special influence of free ammonia during precipitation was investigated in the following experiments. Definite volumes of magnesium nitrate solution were drawn from a burette into a platinum dish, ammonium chloride (10 grms.) was added, the magnesium was brought down by dilute ammonia in presence of microcosmic salt, and strong ammonia equal to one-third the volume of the solution was added. The solutions, after standing, were filtered off on asbestos under pressure in a perforated crucible, and the precipitates were washed with ammonia diluted to the proportion of three parts of water to one of ammonia, dried after moistening with a drop of saturated solution of ammonium nitrate, ignited, and weighed. The results are given in Experiments 1 and 2 of Table IV. In these determinations the mean error reaches +0·0183 grm. in terms of magnesium pyrophosphate; while in Experiments 3 and 4—made similarly, excepting that the supernatant liquid was decanted from the precipitate first thrown down, the precipitate dissolved in hydrochloric acid, and after dilution re-precipitated by dilute ammonia immediately supplemented by enough strong ammonia to make one-fourth the volume of the entire solution—the error amounts in the mean to +0·0061 in terms of the pyrophosphate.

In Experiments 1 and 2 the precipitate was influenced by an excess of microcosmic salt, ammonium chloride, and free ammonia in large amount; in Experiments 3 and 4, by decanting in the manner previously described, by dissolving the precipitate, and re-precipitating, the effects of an excess of microcosmic salt and ammonium chloride are reduced to a minimum, and, in a comparison of the results with those of Experiments 11 and 12 of Table III. the tendency of the free ammonia comes to view. The results discussed seem certainly to point to a general tendency on the part of free ammonia, ammonium chloride, and excess of the phosphate to produce a salt rich in ammonia and deficient in magnesium, which for a definite amount of magnesia precipitated must leave upon ignition a residue weighing more than the normal phosphate.

If it be assumed that a salt of the symbol $(NH_4)_4Mg(PO_4)_2$—the next natural step to the normal salt NH_4MgPO_4—is present in the precipitate, the residue which such a salt would leave upon ignition would be the metaphosphate $Mg(PO_3)_2$. From the relations of the symbols for magnesium pyrophosphate and magnesium metaphosphate, the weight of the residue obtained, and the weight of the pyrophosphate theoretically derivable from the weight of magnesium salt used, it is possible, of course, to calculate the proportionate amounts of pyrophosphate and metaphosphate present in any ignited residue. Proceeding in this manner, it appears that, in order to account for the variations noted, it is necessary to assume the presence in many cases of very considerable amounts of the metaphosphate. Thus, in the case of those results obtained according to the usually accepted method of precipitating and washing with strongly ammoniacal liquids, viz., in Experiments 1 and 2 of Table IV., the proportion of metaphosphate needed to account for the observed error reaches 10 per cent.

(To be continued).

PRESIDENTIAL ADDRESS
TO
THE IRON AND STEEL INSTITUTE.

By Professor Sir W. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S.

The announcement that Her Majesty the Queen will be graciously pleased to accept the Bessemer Medal for 1899, in commemoration of the progress made in the Iron and Steel Industries during Her reign, will be received with enthusiasm throughout the Empire. What the progress has been it will be my privilege to indicate in this address; for your last President of the century, in bidding it a respectful farewell, must offer the best retrospective tribute he can to the grandest industry in the world's history.

This address will, therefore, be mainly devoted to the consideration of British efforts in connection with iron and steel. I shall hope on another occasion to pay homage to the services rendered in other countries to our branch of metallurgy, but in view of our Autumn Meeting last year at Stockholm, I cannot proceed further without making a brief reference to Sweden. To her scientific men our debt is great and of long standing, for we have profited by their labours from the eighteenth century until now. We appreciated the interest in our proceedings which was shown by the presence of His Majesty the King and the Royal Princes at our meetings in the Riddarhus. The gracious kindness of His Majesty during the magnificent reception at his palace of Drottningholm will never be forgotten by those of us who were present. The spontaneous warmth of our reception by the Swedish people also touched us deeply, and the memories of our visit will be handed down as traditions to future members of our Institute, who, in the days to come, will, we trust, again seek the aid of Sweden by supplementing the ores of our own possessions with those from within the Arctic circle.

It seems strange to us now to be reminded that when the nineteenth century dawned the primitive home of the iron industry in Surrey and Sussex had not been abandoned. From my Surrey garden I look towards the tract

once covered by the great forest of Anderida, within the bounds of which coal has recently been discovered. The survivors of the ancient trees of Andreds Wald still give shelter to a few charcoal-burners, the pursuit of whose occupation connects us with the past. There is almost within sound of me, as I write, a stream that fed one of a series of hammer-ponds, and the district within sight is believed to have furnished the coffer for the Doomsday Book, and it certainly did the iron which encircles the cathedral of our great city. The domain has further claim to remembrance, for it supplied guns for the cruisers of Drake and Frobisher. In 1740 there were four more blast-furnaces in Sussex than in any other county; in 1800 there were still two at work, and the one at Ashburnham survived until 1828, producing iron for which the claim was made that it was "in no wise inferior to the Swedish metal." These old charcoal-furnaces could rarely have exceeded 28 feet in height, with an output of some 20 tons a week. Even the greatly improved furnaces adopted about the year 1839, by John Gibbons in South Wales, did not exceed 40 feet in height. Although they were considered to be "enormous," they did not make more than 120 tons weekly. As the century closes, some of their gigantic successors, such as those possessed by our Vice-President, Mr. Andrew Carnegie, produce *daily* no less than 748 tons of iron, and much of the material which issues from them is destined to undergo complex and varied methods of treatment.

From a hill near me I can look over most of the southern home of the iron trade, and I have lingered in the reference to it because a similar comprehensive glance over the landmarks of our industry is all that time will permit me to offer you. Compared with the long past of the simple methods of extracting iron from its ore which in the South of England preceded the use of even charcoal-furnaces, the duration of modern and complex methods seems to be little more than an episode. The age of steel has not as yet endured fifty years, and tracing its rise shows that the entire history of our industry, like that of humanity, is an account of its continual changes. How did progressive development—that is, a change from the relative uniformity of primitive direct reduction processes to those of relative complexity—take place? The change is mainly due to the efforts of individuals stimulated by the country's needs. It was effected by a few men who had the courage to lay aside traditions which had been handed on for generations, and possessed the determination to make costly and laborious experiments for themselves. They were men who, being untrammelled by precedent, called in question the utility of established usages, and their endurance enabled them to solve in a new way problems of vast metallurgical importance. How could the leading British ironmasters of the first half of the nineteenth century be hindered by conventionalism when their mission was to shape the industrial life, not only of their country, but of the world? Progress was made by intellects such as our country has always had in her hours of industrial need. Both the technical workers and the experimenters in the domain of pure science were inspired by the spirit of progress, and their aim was identical. Hence the blending of efforts. Watt, Stephenson, and later Bessemer, Siemens, and others of our own body, became Fellows of the Royal Society, while a Chancellor of the University of Cambridge, and founder of the Cavendish Laboratory, was chosen as first President of the Iron and Steel Institute.

With unity of aim came diversity of method; the scientific investigator devoted himself mainly to the study of molecular problems, while the industrial worker applied his energies to dealing with iron and steel in the mass. This division of labour and unity of purpose is well maintained, and it will be my object to show how beneficial it has been and still is. At every great stage of our progress the industrial worker had an investigator of pure science close at hand.

From the technical point of view, as the eighteenth century closed, a new era in the metallurgy of iron had already begun. Abraham Darby had successfully introduced the use of coke in the blast-furnace; James Watt had, by his powerful engines, much facilitated the production of blast, and had greatly stimulated the out-turn of pig-iron. Nevertheless, the total annual production of pig-iron in the year 1799 did not exceed some 150,000 tons. From the scientific point of view the situation was one of singular interest. The early writers held that good and bad qualities might be inherent in the iron itself. Pliny points out how greatly the properties of iron depend upon its treatment, but he thought that as for the kinds of iron, they were many, and all were distinct, and the first difference arises from the diversity of the soil and climate where the mines are found. But Pliny's view survived far into the present century, and evidence of it lingered in the effective and graceful speech in which the Member for Merthyr proposed a vote of thanks to our first President on the delivery of his Inaugural Address. Mr. Fothergill said then that "thirty years ago the idea prevailed universally . . . that good iron was to be found in certain localities, and could be procured from no other place; it was found good in one place and bad in another." He adds: "Enlightened progress of the last thirty years has shown that the quality of iron depends upon the alloy with which it is mixed."

Enduring as the old view as to the influence of locality was, an experimental basis for a more accurate one had been established very shortly before the present century began, and some, at least, knew that the properties of iron depended on the presence or absence of certain other elements. This position was clearly established by the great Swedish chemist, Bergman of Upsala, who had shown that carbon is the element to which steel and cast-iron owe their distinctive properties. He had initiated the employment of calorimetric methods in determining the properties of iron and steel. He insisted that the real difficulty is to explain how it is that the presence of 0·5 per cent of carbon in iron enables the metal to be hardened by quenching from a red heat, or, in his own expressive words, *Ceterum quomodo dimidia centesima, plumbaginem efficiens, tantam provocare possit differentiam, nodus est gordius haud facile solvendus.* Bergman, moreover, anticipated the later phases of modern research by claiming that iron is a polymorphic element, and plays the part of many metals. In this early view as to the allotropy of iron it should be remembered that in 1790 our countryman, James Keir, followed him closely by urging, before the Royal Society, that what we now call passive iron "is really a distinct form of iron, the alteration being produced without the least diminution of its metallic splendour or change of colour."

Clouet's celebrated experiment on the carburisation of iron by the diamond followed. Doubts, however, were not finally set at rest until 1815, when Pepys, a working cutler in London, excluded the possibility of the intervention of furnace gas. But, as soon as the present century had well turned, the industrial world was in possession of the fundamental fact that carbon is the element of dominant importance in relation to the metallurgy of iron. Well might Bergman express astonishment at the action of carbon on iron. Startling as the statement may seem, the destinies of England throughout the century, and especially during the latter half of it, have been mainly influenced by the use of steel. Her steel rails seldom contain more than Bergman's half per cent of carbon. Her ship-plates, on which her strength as a maritime powder depends, contain less than half that amount. It is essential that the significance of this fact should be clearly understood. Our national existence has long depended on iron and steel. They have been the source of our wealth, one of the main elements of our strength, one cause of our maritime supremacy. Hardly a step of our progress or an incident of our civilisation has not, in one way or another, been influenced by the properties of iron or steel. It is remarkable that these

properties have been determined by the relations subsisting between a mass of iron, itself protean in its nature, and the few tenths per cent of carbon it contains. These properties are, it is true, modified either by the simultaneous presence of elements other than carbon, or by the thermal or mechanical treatment of the mass. The growth of our knowledge of the facts constitutes a large section of our scientific and industrial history. The question arises—Was our national progress delayed by the unreadiness of the technical world in England to take advantage of the facts that science had established?

If we consider the position from the point of view of two remarkable men who were looking for the dawn of the nineteenth century as we are for that of the twentieth, we shall, I think, be satisfied that our progress received no check from failure of industrial workers to assimilate the teaching of science. These men were Black and Cort. Of the scientific men then living, the greatest chemist was Black, Professor at the University of Edinburgh, whom Lavoisier had generously acknowledged as his master. Black fully recognised the importance of Bergman's work, and on his own part insisted on the importance of what would now be called the change in molecular energy as the physical basis on which the properties of iron and steel depend. Black, moreover, in his public lectures gave a singularly accurate description of the process of decarburising iron called "puddling," and devised by "a Mr. Cort," with the results of whose work Black was soon to become familiar. Considering how recent the knowledge of the meaning of oxidation really was at the time, Black's statements with regard to the theory of puddling are truly remarkable. Later on he furnished the Government with an elaborate report on the quality of the material obtained by puddling. He showed, by such mechanical tests as the experience of the time suggested, the superiority of puddled iron, and pointed out that it was more suitable than foreign iron for the appliances "on which," as he says, "the lives of our seamen and the safety of our ships have hitherto mainly depended."

1799. At the end of the century we are justly proud of our Colonial possessions, and are satisfied that the varied applications of iron and steel will enable us to knit together all parts of the Empire. At the beginning of the century Lord Sheffield, in his "Observations on the Commerce of the American States," writing in the early days of Cort's process, shows that it would help to make British iron as cheap as the foreign, an event which he considered would be more advantageous to England than the possession of her American colonies. Black died in 1799, Cort survived till 1800, so that, as the eighteenth century closed, the most eminent scientific man and the foremost practical metallurgist of the generation stood side by side. To Cort we owe the greatest technical advance the modern world had seen; to Black, the recognition of the importance of molecular energy in relation to metallurgical problems.

1800. The production of pig-iron in this country also received a great stimulus from the discovery by Mushet, about the year 1800, that the large deposits of blackband ironstone could be utilised. The century opened with, in round numbers, an annual production of pig-iron not exceeding 200,000 tons, of which less than one-third was converted into bars and other descriptions of wrought-iron. The capital invested was under five millions, and employment was furnished for nearly 200,000 people.

1803. Returning to the scientific aspect disclosed at the dawn of the century, the year 1803 was an eventful one for science. Nevertheless the impulse given to research was not in the most favourable direction for the advancement of metallurgic art. The influence of a small proportion of carbon on iron had been recognised, but the quantitative relation between the iron and the carbon was only considered as bearing on the nature of the product, and not at all from the point of view of chemical union. When, therefore, in 1803, Claude Louis Berthollet published his "Essai de Statique Chimique," it appeared that the action, of what for the moment I may be permitted to classify as the action of *traces* upon *masses*, was in a fair way to be elucidated for the following reason:—Berthollet pointed out that "in comparing the action of bodies on each other which depends on their affinities and mutual proportions, the influence of mass has to be considered." Unfortunately in succeeding years the views of Prout, the courteous opponent of Berthollet, prevailed, mainly through the powerful aid of Dalton, who published also in 1803 his first table of atomic weights. Hence the phenomena which could not be attributed to fixed atomic proportions were set aside and usually neglected. Evidently the action of one-tenth per cent of carbon on iron could not be explained by the aid of combining weights. The century was more than half over before a school of eminent chemists arose, who did not insist that matter is minutely granular, but in all cases of change of state made calculations on the basis of work done, viewing internal energy as a quantity which should reappear when the system returns to its initial state.

1802-7. The production of cast-iron and bar-iron was rapidly increasing, and the suitability of cast-iron and bar-iron for the construction of bridges became evident to engineers, among whom Telford was pre-eminent. A distinguished professor, a worker in pure science, came, in the person of Dr. Thomas Young, to the aid of the technical worker. The need of studying the mechanical properties of iron and steel was evident, and Young showed that the work done in permanently extending or in compressing iron or steel could be represented by a coefficient, to which he gave the name of the "Modulus of Elasticity." This coefficient has probably rendered more service in the development of the study of the strength of iron and steel than any other which has been determined. It is of great importance, because upon it depends the deflection which a structure will take under strain. Young, evidently with a view to bring home evidence as to the great rigidity of steel, gives in his original paper a quaint illustration. He therein shows that if "Hook's law holds" a hanging rod of steel would have to be 1500 miles long in order that the upper portions of it might be stretched to twice their original length. I would incidentally point out that, on the basis of Young's calculation, such a column 1500 miles high, if it were 1 ft. $2\frac{4}{10}$ inches in diameter, would represent the output for the past year of Bessemer steel in this country alone. Statements of this kind had such a singular fascination for Sir Henry, that I have permitted myself a brief departure from chronological order in offering this one.

1817. In the year 1817 the patent was granted to the Rev. Robert Stirling, the specifications of which showed that he had a clear conception of the "regenerative principle," which, applied to furnaces, as will be shown later, has been so fruitful in connection with the manufacture of steel.

1818. In the year 1818, Samuel Baldwin Rogers substituted "iron bottoms" for the sand ones which had been introduced by Cort in the puddling-furnace. I find in the work on "Iron Metallurgy" by Rogers, published in 1857 (but apparently embodying much information he had promulgated in 1818), the statement that his "principal aim" in proposing the use of iron bottoms for puddling-furnaces was "to work the iron in a bath of cinder." He also suggested the use of a flux of a very basic character, and he adds the very interesting statement that use of "the proposed flux will rapidly remove the metalloids from the iron." He pointed out that "the metalloids were removed in the shape of oxides, and combined with the cinder in the puddling-furnace." The actual result was to greatly improve the quality of British iron, and therefore Rogers deserves recognition, which has hardly been accorded to him, as a pioneer of the great basic process of dephosphorisation.

Between the years 1800-4 the amount of foreign iron annually imported was 40,200 tons, and one consequence

of the improved method of puddling was to greatly diminish the importations, which in the period 1823 to 1830 fell to 17,015 tons a year.

1820. In the year 1820 malleable iron began to replace wood for the manufacture of colliery rails, mainly through the efforts of Birkenshaw.

The first quarter of the century did not draw to an uneventful close, for Faraday, working with Stodart, an eminently practical man, gave (in 1820) a stimulus to the study of alloys, and produced the first specimen of nickel steel. In a letter to De la Rive dated April 20, 1820, Faraday writes:—"Mr. Stodart and myself have been engaged in a long series of experiments and trials on steel, with the hope of improving it, and I think we shall in some degree succeed." Later on he writes:—"If you knew the labour of the experiments you would applaud us for our perseverance at least."

1822. In the year 1822 Faraday pointed to a fundamental difference between hard and soft steel, the latter yielding a "carburet of iron" when treated with hydrochloric acid, while hardened steel dissolves completely.

1828. Early in the second quarter of the century notable progress was made, for on the 3rd of March, 1828, James Beaumont Neilson enrolled his patent for the application of the hot-blast to furnaces. It has been suggested by two of my predecessors in this chair that the introduction of the hot-blast might be characterised as a "lucky hit." Viewing, however, the merits of Neilson's great invention in relation to general metallurgical progress, it will be evident that exception may be taken to this suggestion. Neilson's contemporary, David Mushet, held that the introduction of the hot-blast "marked one of the grandest epochs in the history of the manufacture of iron," and he urged that the discovery was the more remarkable as being opposed to received opinions and prejudices, "it being universally held that the blast should be kept as cold as possible." Neilson was an enthusiastic student in Anderson's College, Glasgow, and his strenuous advocacy of technical instruction proved him to be singularly in advance of his age; he was also an ardent experimenter. Moreover, he clearly says he was led to think that "if air was increased in volume by heat, it might be enabled to do more duty." In a sense he was right, for the expansion of the air, though perhaps it was not so important as he thought, represents one-third of the energy contributed by the intervention of the hot-blast stove. That his invention owed anything to "luck" was evidently not the opinion of our own Royal Society, of which body he was elected a Fellow in 1846, as the discoverer of the "hot-blast system of manufacturing iron," and as being "distinguished for his acquaintance with the science of mechanical philosophy." The practical results of the hot-blast were marked, and in the ten years which followed the introduction of his invention the production of pig-iron in this country was more than doubled. The history of the period is singularly interesting.

1842. A patent of June 9, 1842, embodies the first drawing of the perfected single-acting steam-hammer. Such hammers had been proposed by James Watt in 1784, and sketched by Deverell in nearly its present form in 1806.

1843-48. At this time a great investigator appeared in the person of Dr. Thomas Andrews of Belfast, the application of whose great work on the heat of combination will be referred to later.

(To be continued).

Formation of Alums by Electrolysis.—Jas. Lewis Howe and E. A. O'Neal.—Solutions of metals in the lower state of oxidation were electrolysed in a platinum dish, which formed the positive electrode, in presence of sulphuric acid and the different alkali sulphates. The rubidium and cæsium iron alums and the rubidium and cæsium cobalt alums were prepared in this way.—*Journ. Am. Chem. Soc,*

NOTICES OF BOOKS.

Liquid Air and the Liquefaction of Gases. History, Theory, Biography, Practical Applications, Manufacture. By T. O'Conor Sloane. Illustrated. New York: Norman W. Henley and Co. 1899. Pp. 365, 12 mo.

This timely work aims to tell the history of the liquefaction of gases during the last century, and treats the subject from the biographical as well as the scientific standpoint. The author is already known by his works "Electricity Simplified," "How to Become a Successful Electrician," "Electric Toy Making." and the more voluminous "Standard Electrical Dictionary," which has passed to a second edition.

In the book under review Dr. Sloane explains in simple language the fundamental facts of the physics of gases, the measurement of heat by divers kinds of thermometers, the relations of heat to gases, and the physics and chemistry of the air; he then takes up the experimental researches on the liquefaction of gases made by Faraday, and all his successors to the present time. Dealing with the subject historically he introduces in their proper place a notice of the Royal Institution, and biographical sketches of those who have successively held the chair of chemistry therein, from Davy to Dewar. The contributions of Northmore, Cagniard de la Tour, Colladon, Thilorier, Natterer, and Andrews to the liquefaction of gases, are duly explained, and the divers forms of apparatus are shown in illustrations. The writer of this review knows of no work or treatise that contains so full and accurate accounts of the lives and services of Raoul Pictet, Louis Paul Cailletet, Sigmond von Wroblewski, Karl Olszewski, James Dewar, and the American inventor Charles E. Tripler. Dr. Sloane remarks in the preface that the "personal friendship of that wonderfully endowed scientist, Raoul Pictet, one of the fathers of liquid air, poet, musician, physicist, chemist and mathematician, a veritable Admiral Crichton," brought about by writing the book, fully justified the labour bestowed upon it. The volume contains good portraits of Faraday, Pictet, Cailletet, Dewar, and Tripler. Of the latter Dr. Sloane writes: "While Dewar, working on the lines laid down years before by Pictet and assisted by liberal gifts from one of the London Guilds and from private individuals, liquefied gases at great expense, here in the metropolis of the United States, a private individual has erected a plant at his own expense, and for years has liquefied air on a scale which Dewar and his associates never dreamed of. In order to preserve liquid air Dewar devised his celebrated vacuum bulb, an apparatus of the highest merit. Tripler took common tin cans, lined them with felt, filled them with two to five gallons of liquid air, and sent them off hundreds of miles by rail." Linde, with his peculiar apparatus, secured three quarts of liquid air per hour, in May, 1895. Dr. Hampson's apparatus is said to work on the same lines as that of Linde.

Chapter xvii. is devoted to Pictet's experiments in frigotherapy; he found that immersion of his body for eight minutes in a well reduced to the temperature of $-110°$ C. ($-166°$ F.) cured him of long standing dyspepsia. Dr. Fish Clark, of New York, has removed cancer, bunions, corns, warts, and superfluous hair by the application of solid carbon dioxide. The author reviews the applications of liquid air to industrial uses, as an explosive, in electric power work and as a reservoir of energy.

The volume can be recommended to all interested in the wonderful progress of our knowledge of the physics and chemistry of gases. It is pleasantly written, but the author sometimes repeats himself, a blemish to be eliminated in a second edition. Owing to carelessness of the printer and publisher the running head lines of the 365 pages do not change, whereas each chapter should have given to the pages an independent head-line. This defect is by no means peculiar to Dr. Sloane's excellent volume, nor can it be said to detract from its scientific value.

H. C. B.

Notes on Volumetric Analysis. By ARTHUR THORNTON, M.A., and MARCHANT PEARSON, B.A. London, New York, and Bombay: Longmans, Green, and Co. 1898. Pp. 80.

VOLUMETRIC analysis is a most important branch of quantitative chemical analysis; by its means the speed and number of estimations has been enormously increased, and it also affords the student practice in careful manipulation and accurate observation, while at the same time exercising the reasoning faculties. A volumetric experiment can be divided into three sections:—I., *The Principle*, explaining the nature of the reaction and the method of making the solutions; II., *The Method*, which gives full instructions how to conduct the experiment; and III., *The Record*, which gives a clear statement of the numerical details and of the simple mathematics involved in the problem, the last point being one of considerable importance, as it is frequently found that students can perform the chemical experiment accurately, but cannot work out the results through want of mathematical skill.

The experiments described fully illustrate all the simple processes of neutralisation, oxidation, and iodometry. There is also a short chapter on precipitation methods, such as the use of nitrate of silver.

The book will be found of great practical use, not only to students, but as a laboratory companion.

New York Experimental Agricultural Station, Geneva, N.Y. Report of Analyses of Commercial Fertilisers for the Spring of 1898. No. 145. By L. L. VAN SLYKE. Published by the Station. 1898.

DURING the spring of 1898, 1183 samples of commercial fertilisers, representing 739 different brands, were collected; of these 578 were complete, while certain numbers of the others contained either nitrogen, phosphoric acid, or potash only, or two of these ingredients without the third.

The nitrogen present in the complete fertilisers varied from 0·12 to 8·21 per cent, averaging 2·20 per cent. The average amount found by the Station exceeded the amount guaranteed by 0·16 per cent; the greatest excess was 3·27 per cent.

The available phosphoric acid found varied from 3·69 to 14·28 per cent, and averaged 8·65 per cent. The amount of phosphoric acid soluble in water varied from 0·10 to 11·11 per cent, and averaged 5·08 per cent.

The potash present in the complete fertilisers varied from 0·22 to 15·22 per cent, and averaged 4·91 per cent. In 426 brands of these fertilisers the amount of potash present was above that guaranteed, and in 140 brands it was below. In 110 cases the potash was present as sulphate free from excess of chlorides.

CORRESPONDENCE.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

SIR,—In his letter in the CHEMICAL NEWS of May 19th (vol. lxxix., p. 239) Mr. Hooper says:—"Mr. Pattinson states in his letter that the test-acid on the 32 equivalent is weaker than *the true normal acid.*"

I beg to point out that I did not use the words in italics. I did say, however, "English test-acid is weaker than test-acid made on the correct equivalent of soda," and this statement requires some explanation. Before the use of French weights and measures had become general in laboratories in this country, it was customary in laboratories of alkali works on the Tyne to make the test-acid of such a strength that 592·5 fluid grains, or 59·25 measures on a burette exactly neutralised 50 grains of pure carbonate of soda. With this test acid, the reading of the burette indicated the percentage of soda in a sample when 50 grains of it were operated upon. Now, 50 grains of pure carbonate of soda neutralised by acid made in a similar way, but on the basis of the 31 equivalent of soda, requires only 58·49 measures of such acid. The English test-acid made in this way on the 32 equivalent is therefore weaker than the acid similarly made on the 31 equivalent. As I did not explain in my previous letter how the test-acid used to be made, I think Mr. Hooper is to be excused for having misunderstood me.

Mr. Hooper, however, still does not see that my tables quoted and extended by Dr. Lunge are quite correct. They do just what they profess to do—viz., give the equivalent in English alkalimetrical degrees of any real percentage of soda. In other words, they state what the test would be if actually made with English test-acid.

Mr. Hooper makes some calculations based on the assumption that "a normal acid which saturates 54 parts of Na_2CO_3 *will neutralise* 41 *parts NaHO or* 32 *parts* Na_2O." He will see that this assumption is wrong if he considers the amount of sulphuric acid in a normal acid that saturates 54 parts Na_2CO_3. Such an acid contains 49·924 grms. H_2SO_4 per litre, and will saturate 54 grms. of Na_2CO_3, or 40·75 grms. (not 41 grms.) of NaOH, or 31·585 grms. (not 32 grms.) of Na_2O. One c.c. of it is therefore equivalent to 0·054 grm. Na_2CO_3, 0·04075 grm. NaOH, or 0·031585 grm. Na_2O. 4·1 grms. of caustic soda therefore require for neutralisation, *not* 100 *c.c.*, but $\frac{4{\cdot}1 \times 100}{4{\cdot}0} = 100{\cdot}61$ c.c.; or stated in terms of soda, Na_2O, 3·2 grms. of caustic soda would require $\frac{100{\cdot}61 \times 3{\cdot}2}{4{\cdot}1} =$ 78·52 c.c.; that is to say, pure caustic soda actually containing 77·5 per cent of soda will, when tested with English test-acid, indicate 78·52 English alkalimetrical degrees of soda.

If Mr. Hooper will only make some English test-acid as prescribed by Dr. Lunge and test some caustic soda with it, he will prove experimentally that the tables are quite correct.—I am, &c.,

JOHN PATTINSON.

75, The Side, Newcastle-upon-Tyne,
May 24, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., July 11, 1898.

Research on Optical Activity.—L. Tschugaeff.—The author has studied the variations in the rotatory power of the homologous series, principally of the aromatic ethers of menthol.

Presence of Di-isopropyl in the Ether of Baku Petroleum.—O. Aschan.—Already noticed.

On the Acetals of Acrolein and of Glyceric Aldehyde.—A. Wohl.—Acetal of chloropropionic aldehyde is easily obtained by saturating two volumes of cold absolute alcohol—to which is added, little by little, one volume of acrolein, with hydrochloric acid gas. It separates in the form of a heavy oil, which is treated with dry bicarbonate of soda, washed with water, and dried over K_2CO_3. One part of this raw acetal has then added to it two parts of powdered

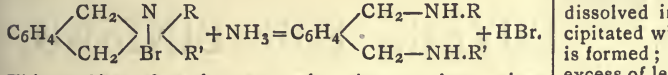
KOH, and the whole is distilled between 125° and 130°; the distillate is fractionated a second time, and is then practically pure acetal of acrolein, $CH_2=CH.CH(OC_2H_5)_2$. It is in the form of a mobile liquid, having an agreeable odour, slightly soluble in water, and boiling at 125·5°. The acetal of glyceric aldehyde is prepared by heating the acetal of oxychloropropionic aldehyde for several hours with an aqueous solution of K_2CO_3, or by oxidising acetal of acrolein in suspension in water by $KMnO_4$ at 10 per cent in the cold, 2—3°. Solid K_2CO_3 is added to the filtrate, the acetal is isolated by means of ether, and purified by distillation in vacuo.

The Isomeric Chlorides of *o*-Sulphobenzoic Acid, and on an Interesting Case of Tautomerism.—R. List and M. Stein.—The authors undertook this investigation before the publication of M. Remsen's results, and, as far as concerns dissymmetry, they have obtained very different results, as shown in this paper. The chlorides in question each react as if they were tautomers, and, further, they cannot be transformed one into the other. The one melting at 79° reacts less easily than the one melting at 40°; thus the author has called them respectively the stable and instable chlorides.

Condensation of Salicylic Aldehyde with the Acid Amides.—F. Cebrian.—Salicylic aldehyde condenses with the acid amides with elimination of water: $C_6H_4<^{OH}_{CHO} + R.CO.NH_2 = C_8H_6O_2NR + H_2O$. Acetamide, formamide, and benzamide act the best. The products of condensation are amorphous powders, not very soluble as a rule except in cold dilute alkalis.

The Semicarbazone of α-Ionone.—F. Tiemann.—The product of the action of H_2SO_4 on pseudo-ionone contains a mixture of pseudo-ionone, ionone α, and ionone β. This mixture is heated with alcoholic KOH, to decompose the uncondensed pseudo-ionone. The two isomeric ionones are then caught by a current of steam and transformed into semicarbazones by means of the chlorhydrate of semicarbazide and acetate of sodium. The mixture of the two semicarbazones is crystallised several times in absolute alcohol; the first portions consist of pure semicarbazone of β-ionone. The mother-liquors are treated with H_2SO_4, then by hydrochlorate of hydroxylamine; the oxime α which is deposited is decomposed by an acid, and the ionone α regenerated in a state of purity. The semicarbazone of α-ionone melts at 138° after several crystallisations in dilute alcohol.

On the Derived Bases of Xylylene-diamine, and on a Nucleus with Eleven Links.—M. Scholtz.—The action of NH_3 at a high temperature on quaternary bromides causes the replacement of the bromine by the NH_2 group, and the simultaneous migration of one of the alcoholic radicals, thus—

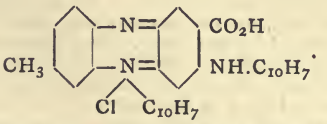


This reaction takes place even when the secondary amine, $NH<^{R}_{R'}$, is a cyclic base, such as piperidine.

The Use of Bromide of *o*-Xylylene for Detecting the Bases.—M. Scholtz.—A continuation of the research on the action of bromide of *o*-xylylene on the primary, secondary, and tertiary fatty and aromatic amines. The author divides the amines into eight groups, which are here described.

Nitrophenols derived from the Bromoparatoluidine of Wroblewski [$C_6H_3Br(CH_3).NH_2$. 1 : 2 : 3].—J. T. Hewitt and H. E. Stevenson.—The authors describe the preparation and properties of bromotolunitrophenol, bromotolunitro-α-naphthol, and bromotolunitrosalicylic acid.

The Action of α-Naphthylamine on Bromo-tolunitrosalicylic Acid.—J. T. Hewitt and H. E. Stevenson.—By the action of α-naphthylamine on bromotolunitrosalicylic acid an atom of bromine is separated, and a difficultly purified halogen body is formed. This is dissolved in alcoholic KOH, then precipitated with water. The acetic solution of this precipitate is treated with concentrated hydrochloric acid, and a crystalline hydrochlorate is obtained, having a violet colour, and answering to the formula $C_{34}H_{24}ClN_3O_2$. The energy with which the acid is combined in this substance points to the following constitution:—

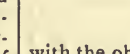


The corresponding base has not been isolated, but its different salts—bromide, iodide, nitrate, sulphate—have been obtained; they are insoluble in water.

Note on Nitrophenine.—J. T. Hewitt and H. E. Stevenson.—The authors consider that the symmetric formula given to this body by Fischer and Hepp is inadmissible. This is confirmed by a direct experiment with hydrazophenine. The denitration of this body gives a negative result. Hydrazophenine does not contain a primary amine group.

Physico-chemical Study of the Salts of Diazonium. Hydrate of Diazonium and the Normal Diazoïcs.—W. B. Davidson and A. Hantzsch.—The authors have made a large number of determinations of electrical conductivity and heats of neutralisation, and have succeeded in showing that in its salts diazonium behaves like ammonium, while the hydrate of dinitrobenzene, treated with an alkali, gives off a quantity of heat, such as would be afforded by a strong acid under the same conditions.

On the Action at a Distance of Substituted Groupings in the Tetrazolium Nucleus.—E. Wedekind and L. Strauwe.—The authors have made a comparative study of a series of formazoylic derivatives,—



with the object of establishing the influence of the groups R, *x*, and *y* on the facility of oxidation of these compounds. The group R has far the greater influence.

Journal de Pharmacie et de Chimie, Series 6, Vol. ix., No. 3.

On Anabsinthine: a New Substance derived from Absinth.—MM. Adrian and Trillat.—This substance is prepared by making successive alcoholic extracts of the plant; these are evaporated down, and after a preliminary filtration a chloroformic extract is made. This extract is dissolved in boiling alcohol, and the organic matter precipitated with acetate of lead, until no further precipitate is formed; filter cold, and add tartaric acid to remove the excess of lead salt, and filter again. The extract resulting from the complete evaporation of the alcohol is washed with water until no longer acid; dry, and when warm add one part of rectified benzene. On cooling we obtain, after some days, a crystalline mass, which is left to drain, and washed with cold benzene. This is dissolved again in boiling alcohol, and, on the addition of a little water, the crystals again appear at the end of half-an-hour. These crystals are anabsinthine; they take the form of long, white, prismatic needles. The formula given to this product is $C_{18}H_4O_4$; this formula has been confirmed by cryoscopic means. If dried at 120°, the fusing-point of anabsinthine is 258—259°; after being exposed to the air, this falls to 236—238°: it is slightly soluble in water, and more so in alcohol, benzine, and chloroform. It crystallises in acetone in magnificent crystals, the facets of which may reach 1 c.m. in width—a veritable crystallographic curiosity.

MISCELLANEOUS.

Opening of the Dronfield Sewage Works.—The new sewage disposal works of the Dronfield Urban District Council recently opened, have been completed in accordance with the design of the Council's engineer, Mr. G. White, C.E., of Mexboro', and are on the international system, comprising Candy circular upward flow tanks with automatic sludge or detritus removal apparatus, clarifiers, and polarite oxidising filter-beds—now popularly termed bacteria beds. The scheme has been carried out in accordance with the plans approved by the Local Government Board, the contractors being Messrs. Margerrison and Sons, of Dronfield.

Purdue University.—This University embraces six departments of instruction, the courses of each extending through four years. They are Mechanical, Civil, and Electrical Engineering, Applied Sciences, Agriculture, and Pharmacy. In addition to the regular instruction there will now be given a series of lectures on different departments in the organisation of railways. American railways are entering upon a period of development, the conditions of which are more exacting than any they have hitherto experienced. The volume of traffic is increasing enormously, and increased speed is constantly demanded; this necessitates more and more attention to the question of safety, and therefore a demand for men who are thoroughly trained for the service. Purdue University has for several years offered work covering a considerable variety of railway subjects, but recently the plan has been revised, new subjects added, and consequently a department of railway engineering and management formed.

Royal Institution.—An adjourned General Meeting of the Members of the Royal Institution was held on the 22nd inst., His Grace the Duke of Northumberland, President, presiding, when the following foreign scientific men were elected Honorary Members, in commemoration of the Centenary of the Royal Institution, which will be celebrated on the 5th, 6th, and 7th of June next:—Professor S. Arrhenius (Stockholm), Professor C. Barus (Brown University), Professor H. Becquerel (Paris), Professor G. L. Ciamician (Bologna), Professor N. Egorof (St. Petersburg), Professor A. P. N. Franchimont (Leiden), Professor A. E. Gautier (Paris), Professor H. G. Kayser (Bonn), Professor W. Körner (Milan), Mr. S. P. Langley (Washington), Professor G. L. Van der Mensbrugge (Ghent), Professor A. A. Michelson (Chicago), Professor H. Moissan (Paris), Professor R. Nasini (Padova), Professor W. Nernst (Göttingen), Professor W. Ostwald (Leipzig), Dr. E. Solvay (Brussels), Professor R. Thurston (Cornell), Professor E. Villari (Naples), Professor J. L. G. Violle (Paris), Dr. E. Ador (Geneva), Dr. L. Bleekrode (The Hague), Professor J. S. Ames (Johns Hopkins University), Professor G. F. Barker (Philadelphia), Dr. O. Liebreich (Berlin), Dr. W. L. Wilson (Washington).

New Method of Detecting and Estimating Acetone in Water, and in the Methylic and Ethylic Alcohols.—G. Denigès.—To detect acetone in—(A) *Aqueous solution*, 2 c.c. must be mixed with 2 c.c. of a mercuric reagent (dissolve 5 grms. of mercuric oxide in a hot mixture of 20 c.c. of sulphuric acid and 100 c.c. of water); plunge into boiling water; if after ten minutes' boiling there is no cloudiness or precipitate, acetone is not present; if, on the contrary, acetone is present, the amount of precipitate or cloudiness is in proportion to the amount of acetone: the precipitate, however, is never seen in less than forty-five seconds. In (B) *Methylic solution*, proceed as before, but add 2 c.c. of methylic alcohol, 2 c.c. of water, and 4 c.c. of mercury reagent; this must be diluted with water, as the undiluted methylic alcohol when heated precipitates the mercuric sulphate: by this process we can detect 3 centigrms. per litre of the original solution. (C) *Ethylic solutions.*—In the case of ethylic alcohol we must have such a dilution that the alcoholic degree of the liquid shall not be more than 2, or else the mercurous sulphate arising from the reducing action of the alcohol will be precipitated on boiling. Thus a solution of acetone in ethylic alcohol at 90° should be diluted to one-fiftieth, and then treated in the same manner as the aqueous solution.—*Journ. de Pharm. et de Chimie*, Series 6, vol. ix., No. 1.

MEETINGS FOR THE WEEK.

TUESDAY, 30th.—Royal Institution, 3. "Recent Advances in Geology," by Prof. W. J. Sollas, D.Sc., F.R.S.
—— Society of Arts, 8. "The Revival of Tradesmen's Signs," by J. Starkie Gardner.

THURSDAY, June 1st.—Royal Institution, 3. "Water Weeds," by L. C. Miall, F.R.S.
—— Chemical, 8. "The Hydrosulphides, Sulphides, and Polysulphides of Potassium and Sodium," by W. Popplewell Bloxam. "On the Relative Efficiency of various Forms of Still-head for Fractional Distillation," by Sydney Young, D.Sc., F.R.S. "The Salts of Dimethylpyrone, and the Tetravalence of Oxygen," by J. N. Collie, Ph.D., F.R.S., and Thomas Tickle.
—— Society of Arts, 4.30. "The Port of Calcutta," by Sir Charles Cecil Stevens.

SATURDAY, 3rd.—Royal Institution, 3. "The Music of India and the East, and its Influence on the Music of Europe" (with Musical Illustrations), by Edgar F. Jacques.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2062.

ON A TUNGSTO-LITHIC TUNGSTATE.

By L. A. HALLOPEAU.

I have already shown in a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xix., p. 746) that hydrogen reduces the alkaline paratungstates at a red heat. With the paratungstates of sodium and potassium we obtain tungsto-sodic and tungsto-potassic compounds—or, as they were formerly called, *tungsten bronzes*. The paratungstate of lithium is reduced more completely and binoxide of tungsten is abundantly formed.

To obtain tungsten bronze with the paratungstate of lithium it is necessary to make this salt react on a reducing agent other than hydrogen.

Scheibler announced the production of quadrangular blue tablets by the action of tin on melted tungstate of lithium. Long afterwards, von Knorre took up the subject. He stated that this blue compound might *perhaps* contain $Li_2W_5O_{15}$.

As all this was not very decisive, I undertook to repeat this experiment and make a careful analysis of the product of the reaction.

Paratungstate of lithium was heated for an hour with a small quantity of tin. The operation was carried out in a porcelain crucible placed in a muffle furnace and heated to bright redness. The melted mass was treated successively with boiling water, concentrated hydrochloric acid, and a boiling solution of lithia at about 20 per cent. After a final washing with warm water, a powder remains, having a very deep blue colour and composed of microscopic prisms. The blue coloration is very intense when the product is freshly made, but it eventually assumes a slightly greyish appearance.

The analysis I made of this substance confirmed the formula $Li_2W_5O_{15}$, which may also be written thus:— $Li_2O,WO_3+WO_2,3WO_3$.

	Found.	Calculated.
Li_2O	2·55	2·56
5W	78·19	78·36
14O	—	19·08
		100·00

From its constitution this body resembles tungsten bronze, $Na_2O,WO_3 + WO_2,3WO_3$, which is also prismatic, and which has been obtained by Philipp by melting an acid tungstate of sodium with tin.—*Bull. Soc. Chim.*, Series 3, vol. xx.-xx., No. 23.

ON THE COMPOSITION OF THE OSMIAMATES.

By L. BRIZARD.

In the year 1847, Fritzsche and Struve (*Bull. de l'Acad. de St. Petersbourg*, vol. vi., p. 81) described the salts of an osmium compound containing nitrogen and oxygen, to which they gave the name osmiamic acid. The analysis of osmiamate of potassium led them to assign to it the formula $Os_2N_2O_5K_2$.

In 1891, M. Joly (*Comptes Rendus*, vol. cxii., p. 1442) took up the study of these compounds. He examined particularly the conditions of the preparation of osmiamate of potassium and the products of its decomposition by heat, and he came to the conclusion that the formula given by Fritzsche and Struve ought to be modified and replaced by $OsNO_3K$. Osmiamic acid would therefore have the formula $OsNO_3H$, and might be considered as the first anhydride of a body $OsNO(OH)_3$ entirely analogous to the hydrate, $RuNO(OH)_3$, already examined by M. Joly. Osmiamic acid and the osmiamates would thus be nitroso-compounds of osmium.

The estimation of the osmium in osmiamate of potash would have removed all doubts, but M. Joly decided to attempt this later on. This estimation, in fact, presents a certain difficulty; it is impossible to use the ordinary method of analysis, which consists of first reducing the material in a current of hydrogen and then isolating the reduced metal by washing with water. In actual practice the osmium remains mixed with the alkali and we cannot effect its separation by means of water, as a part of the metal becomes transformed into a volatile peroxide.

Having undertaken the examination of the action of reducing agents on the nitroso-compounds of the platinum metals, I found it necessary to verify, by a complete analysis, M. Joly's statements on the composition of the osmiamates.

Osmiamate of Potassium.—I prepared this salt by the method given by Fritzsche and Struve, viz., the action of ammonia on a solution of peroxide of osmium in potash, taking the exact proportions shown by the formula $OsO_4+KOH+NH_3=OSNO_3K+2H_2O$. To estimate the osmium, I first precipitated it from the solution of the osmiamate in the state of sulphide, taking the precautions recommended by M. Lecoq de Boisbaudran (*Comptes Rendus*, vol. xcvi., p. 1838), so as to obtain complete precipitation. The osmium is thus separated from the alkali. The reduction of the sulphide obtained by means of a current of hydrogen leaves only osmium as a residue.

I estimated the potassium by reducing the osmiamate in a current of hydrogen, separating the alkali from the osmium by washing with water and then transforming it into chloride of potassium. These analyses gave me the following results:—

	Found.			Calculated.	
	I.	II.	III.	Fritzsche and Struve.	Joly.
Os	65·1	65·2	—	67·1	65·3
K	—	—	13·33	13·76	13·38

Osmiamate of Ammonium.—I prepared this body by the action of osmiamate of silver on a solution of chloride of ammonium. The solution of osmiamate of ammonium thus obtained is sufficiently stable to remain exposed in dry vacuo at the ordinary temperature for several days; it then gives very beautiful crystals, isomorphous with those of the potassium salt (H. Dufet, *Bull. Soc. Min.*, vol. xiv., p. 214; and vol. xviii., p. 419). The reduction of this salt in a current of hydrogen leaves a residue of pure osmium, which can be easily weighed. I have also estimated the ammonia present by Schlœsing's method, and found:—

	Found.		Calculated.	
	I.	II.	Fritzsche and Struve.	Joly.
Os	70·2	—	72·5	70·4
NH_3.. ..	—	6·0	6·4	6·2

Osmiamate of Silver.—This salt, slightly soluble in water, is deposited immediately when we treat a solution of osmiamate of potassium with nitrate of silver at the ordinary temperature. The reduction of this salt in a current of hydrogen leaves a residue of osmium and silver; we can thus estimate the total osmium-silver. I have, further, estimated the silver in the form of chloride of silver by precipitating it with chloride of potassium. I obtained the following results:—

	Found.		Calculated.	
	I.	II.	Fritzsche and Struve.	Joly.
Os+Ag..	82·8	—	84·6	82·7
Ag	—	29·8	30·6	29·9

All these analyses confirm in a very satisfactory manner the predictions of M. Joly, and the composition of osmiamic acid should therefore be represented by the formula $OsNO_3H$. If, further, we compare the action of ammonia on osmiate of potash (which gives the osmiamate) with that of ammonia on ruthenate of potassium, which gives, as I have already shown (*Comptes Rendus*, vol. cxxii., p. 730), a nitroso-compound of ruthenium, we again find a fact supporting the hypothesis that the osmiamates are nitroso-compounds of osmium.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 5.

ON THE COMPLEX SALTS OF PALLADIUM: PALLADOXALATES.

By M. VÈZES.

I HAVE already shown (*Bull. Soc. Chim.*, xix., 875) how the plato-oxalate of potassium, $Pt(CO_2.CO_2)_2K_2+2H_2O$, can be obtained by a simple exchange reaction starting from the corresponding chlorinised salt, the chloroplatinite of potassium, $PtCl_4K_2$. The analogy between platinum and palladium, in as far as concerns the properties of their complex salts, and particularly between the plato-salts, PtX_4K_2, and the pallado-salts, PdX_4K_2, naturally leads us to ask if the same reaction would not enable us to obtain a pallado-salt analogous to the plato-oxalate of potassium.

The existence of the salt is reasonable; Kane (*Phil. Trans.*, cxxxii., 297) in fact announced a "double oxalate of palladium and ammonium" corresponding to the formula $C_2O_4Pd.C_2O_4Am_2+2H_2O$, which he obtained by dissolving freshly precipitated palladous oxide in a solution of binoxalate of ammonia. On the other hand, Fischer (*Pogg. Ann.*, lxxi., 443), by adding, drop by drop, a solution of oxalate of potassium to a solution of palladous chloride, obtained a yellow powder, insoluble in water, which he did not, however, analyse.

I. To a warm concentrated solution of chloropalladite of potassium, $PdCl_4K_2$, we add a concentrated solution of neutral oxalate of potassium, in the proportion of 2 molecules of oxalate for 1 molecule of chloropalladite, The deep coloured solution of this latter salt is partially decoloured, and takes a yellow-brown tint; on cooling it deposits fine dark yellow needles, to which analysis (see later) gives the formula $Pd(CO_2.CO_2)_2K_2+3H_2O$, *i.e.*, a pallado-oxalate of potassium. This salt is thus formed from the chloropalladite by the exchange reaction—

$$PdCl_4K_2+2CO_2K.CO_2K=Pd(CO_2.CO_2)_2K_2+4KCl,$$

similar to the analogous method of preparing the plato-oxalate of potassium.

The same salt can be obtained by another reaction, starting with another pallado-salt—the palladonitrite of potassium, $Pd(NO_2)_4K_2$.

The transformation into pallado-oxalate cannot be effected in neutral solution, but it is possible in acid solution. If, for example, we act on a solution of palladonitrite with an excess of oxalic acid, and bring the mixture to boiling point, the whole of the nitrogen contained in the salt will be set free in the state of nitrous fumes, and the substitution of the oxalic acid for the nitrous acid effected according to the equation—

$$Pd(NO_2)_4K_2+2CO_2H.CO_2H=Pd)CO_2.CO_2)_2K_2+4NO_2H,$$

will give pallado-oxalate of potassium, which crystallises out on cooling.

The salt thus prepared is identical with that obtained in neutral solution by means of the chloropalladite. Now the two reactions we have just mentioned, applied to the chloroplatinite and the platonitrite, give, on the contrary, two different products, the two isomerous plato-oxalates described by Söderbaum (*Bull. Soc. Chim.*, xix., 876); the pale plato-oxalate is formed in neutral solution, and the dark plato-oxalate in acid solution. We may therefore easily conclude, from this fact, that the complication brought into the study of the plato-oxalates by the existence of two isomeric varieties will not be found in that of the pallado-oxalates.

II. The analysis of the pallado-oxalate of potassium prepared by these two methods, and dried in the cold by pressure between filter-papers, has given the following results:—

1. 0·6193 grm. of material, heated to redness with an excess of sulphuric acid, gave a residue weighing 0·4168 grm.; this residue, after washing in cold water, calcination, reduction by hydrogen, and cooling in carbonic acid gas, gave 0·1593 grm. of palladium; the difference, 0·2575 grm., consisted of sulphate of potassium containing 0·1157 grm. of potassium.

2. 0·6874 grm. of material, heated to 80°, lost 0·0923 grm. of water; the residue, calcined as above with an excess of sulphuric acid, gave 0·1781 grm. of palladium and 0·2842 grm. of sulphate of potassium, containing 0·1277 grm. of potassium.

3. 0·9237 grm. of material, heated to redness with an excess of tungstic acid, gave (after passing the liberated gases over copper and oxide of copper heated to dull redness) 204 2 c.c. of carbonic acid gas at 0° and 760 m.m., weighing 0·4013 grm., and containing 0·1094 grm. of carbon.

4. 0·4725 grm. of material also gave 103·0 c.c. of carbonic acid gas at 0° and 760 m.m., weighing 0·2024 grm., and containing 0·0552 grm. of carbon.

	Calculated.		Found.			
			I.	II.	III.	IV.
Pd	105·7	25·53	25·72	25·91	—	—
2K	78·3	18·91	18·68	18·57	—	—
4C	48·0	11·60	—	—	11·85	11·68
8O	128·0	30·92	—	—	—	—
$3H_2O$	54·0	13·04	—	13·43	—	—
$Pd(CO_2.CO_2)_2K_2.3H_2O$—	414·0	100·00	—	—	—	—
$Pd+SO_4K_2$	280·0	67·63	67·30	67·25	—	—
$4CO_2$	176·0	42·52	—	—	43·45	42·84

III. The pallado-oxalate of potassium is easily soluble in warm water, but only slightly so in cold water. It is not very stable under the influence of heat. When the dry salt is kept for a long time at about 80° it loses not only its water of crystallisation, but also a certain quantity of carbonic acid gas and carbonic oxide; at the same time it becomes black, and gives, besides oxalate of potassium, which can be removed by washing, more or less oxidised palladium. Boiling its solutions causes, after a time, an analogous decomposition, which is shown by a slight metallic deposit on the sides of the glass vessel.

Simple reactions enable us to reform the two salts from which the pallado-oxalate has been prepared, viz., the chloropalladite and the palladonitrite: to effect this it suffices to produce the inverse conditions to those which have been described above.

The transformation of the chloropalladite into pallado-oxalate is effected in neutral solution; the return of the pallado-oxalate to chloropalladite takes place in acid solution. It suffices, in fact, to treat the solution with an excess of hydrochloric acid, to see the colour become much deeper; after concentration and cooling, it will give crystals of chloropalladite, mixed with colourless crystals of oxalic acid,—

$$Pd(CO_2.CO_2)_2K_2+4HCl=PdCl_4K_4+2CO_2H.CO_2H.$$

In the same manner the transformation of the palladonitrite into pallado-oxalate takes place in acid solution; the return of the pallado-oxalate into palladonitrite takes place in neutral solution, by the action of an excess of nitrite of potassium,—

$$Pd(CO_2.CO_2)_2K_2+4NO_2K=Pd(NO_2)_4K_2+2CO_2K.CO_2K.$$

These reactions give evidence of the very close relations between these three salts, and thus justify the inclusion of the pallado-oxalate of potassium in the general class of pallado-salts, PdX_4M_2, which comprise nearly all the known saline compounds of palladium. There is, further, some reason for believing that, like most of the potassic pallado-salts, this pallado-oxalate may be the starting-point of a new class of pallado-salts. In fact, M. H. Loiseleur, Professor at the Libourne College, who is at present studying this subject, has already obtained, by double decomposition with nitrate of silver, a well-crystallised pallado-oxalate of silver, and he derived from this salt, by the careful action of hydrochloric acid, a pallado-oxalic acid fairly stable in moderately concentrated aqueous solution, and apparently able to furnish a complete series of metallic salts. The existence of this acid thus furnishes the proof of the complex nature of pallado-oxalate of potassium, and justifies the unitary formulæ which have here been attributed to it.—*Bull. Soc. Chim.*, Series 3, vol. xvi., No. 5.

THE CONSTITUTION OF THE AMMONIUM-MAGNESIUM PHOSPHATE OF ANALYSIS.*

By F. A. GOOCH and MARTHA AUSTIN.

(Concluded from p. 246).

Precipitation by Excess of the Magnesium Salt.

THE relations which obtain in the reverse process of precipitation—the action of the excess of the magnesium salt upon a soluble phosphate—were studied in experiments to be described. A solution of pure hydrogen disodium phosphate was prepared by carefully re-crystallising the pure salt of commerce five times from distilled water in a platinum dish, dissolving the crystals, and diluting to definite volume. The standard of the solution was established by evaporating to dryness in a weighed platinum crucible known volumes of the solution, igniting the residue, and weighing the sodium pyrophosphate. Magnesia mixture, the precipitant, was prepared by dissolving 55 grms. of magnesium chloride in as little water as possible and filtering, mixing with this solution 28 grms. of ammonium chloride purified by treating it in strong solution with bromine water and a slight excess of ammonia, filtering, diluting to 1 litre, and, after standing for some hours, filtering again.

The tests of the following table show that the precipitation of a soluble phosphate by the magnesia mixture is practically complete in faintly ammoniacal solutions even when very dilute and charged with large amounts of ammonium chloride, provided the magnesia mixture is present in sufficiently large excess.

TABLE V.

P_2O_5 in HNa_2PO_4 taken. Grm.	Magnesia mixture. C.m.s.	Volume. C.m.s.	NH_4Cl. Grms.	Precipitation.
0·0005	10	100	—	Visible at once throughout the liquid.
0·0005	50	100	—	
0·0005	10	100	10	
0·0005	10	200	60	
0·0001	50	250	60	
0·0001	10	100	—	
0·0001	10	100	10	
0·0001	50	200	10	
0·0001	10	250	60	Visible after settling out.
0·0001	50	300	60	
0·0001	50	500	60	

This conclusion was further substantiated by an actual test (by the molybdate method) of the ignited residue, obtained by evaporating a filtrate from ammonium-magnesium phosphate (equivalent to 0·8614 grm. of the pyrophosphate) precipitated by a faintly ammoniacal solution of magnesia mixture in presence of 60 grms. of ammonium chloride, which gave a precipitate of ammonium phosphomolybdate yielding 0·0002 grm. of magnesium pyrophosphate. It is evident, therefore, that any considerable deficiences of weight of the magnesium phosphate obtained by precipitating equal amounts of a soluble phosphate by magnesia mixture in presence of varying amounts of ammonium chloride, cannot be attributed to varying solubility of the magnesium phosphate under changing proportions of the ammonium chloride.

The results recorded in Section A of Table VI. were obtained by treating definite volumes of the pure solution of hydrogen disodium phosphate with magnesia mixture, in slight excess above the amount required to bring down the phosphate, and making the solution distinctly ammoniacal. After thorough subsidence, the precipitate was filtered off on asbestos under pressure in a perforated platinum crucible, washed in water faintly ammoniacal, dried, ignited, and weighed. In Experiments 1, 5, and 6, only the ammonium chloride present in the magnesia mixture was used; in the other cases weighed portions were added. In the experiments of Section B, the precipitate was dissolved in hydrochloric acid after filtering off the supernatant liquid, brought down again in dilute solution by ammonia in distinct excess, and thereafter treated as in the experiments of Section A. The experiments of Section C were conducted similarly to 1, 5, and 6 of A, excepting that the magnesia mixture was introduced into the ammoniacal solution of the phosphate drop by drop from a burette. The precipitations in A, B, and C were proved to be practically complete; for by treatment of the filtrates with more magnesia mixture and standing, no more than a trace—0·0001 grm. at the most—of the phosphate was found. The ignited residues never contained more than a mere trace of chlorine.

While the results are not entirely regular, the tendency of the ammonium salt to produce errors of deficiency in proportion to its amount is plain if we compare among themselves the experiments of A upon similar amounts of phosphate, and then those of B upon similar amounts of phosphate among themselves; and by a comparison of corresponding results in A and B it is clearly shown that the presence of an excess of magnesia mixture tends to counteract more or less completely, errors of deficiency due to the action of the ammonium chloride. These facts are quite in harmony with the hypothesis that the ammonium salt tends to produce an ammonium-magnesium phosphate richer in ammonia and phosphoric acid and poorer in magnesia than the normal salt, NH_4MgPO_4; for, though the production of such a salt in presence of an excess of the soluble phosphate compels the combination of a definite amount of magnesium with more than the normal amounts of phosphoric acid and ammonia (as was the case in the former series of experiments), when the supply of the soluble phosphate is limited the amount of magnesium associated with it must fall below the normal (as is the case in the present series of experiments). Moreover, the behaviour of the precipitant is quite in accord with the hypothesis; for, though the influence of an excess of the soluble phosphate would naturally tend (as was observed) in the same direction as that of the ammonium salt and free ammonia, viz., to the production of the phosphate deficient in magnesium, the tendency of an excess of the magnesium salt must obviously be to increase the amount of magnesium in the phosphate, as was observed in the experiments of Table VI. The hypothesis fits the facts, therefore, on both sides; and, if precipitation is practically complete (as was shown to be the case throughout) the argument for the existence of an ammonium-magnesium phosphate — poorer than the normal salt in magnesium — possibly the salt $(NH_4)_4Mg(PO_4)_2$—seems to be strong.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Series 4, vol. vii., No. 39, March, 1899.

TABLE VI.

	$Mg_2P_2O_7$ corresponding to HNa_2PO_4 taken. Grm.	$Mg_2P_2O_7$ found. Grm.	Error in terms of $Mg_2P_2O_7$. Grm.	Error in terms of P. Grm.	Volume. C.m.³.	NH_4Cl in magnesia mixture. Grms.	NH_4Cl added. Grms.	$MgCl_2.6H_2O$ in magnesia mixture. Grms.
				A.				
1.	0·8615	0·8613	−0·0002	−0·00005	150	1·68	—	3·3
2.	0·8615	0·8615	0·0000	0·00000	200	1·68	20	3·3
3.	0·8615	0·8602	−0·0013	−0·00036	200	1·68	20	3·3
4.	0·8615	0·8561	−0·0054	−0·00151	300	1·68	60	3·3
5.	0·0852	0·0862	+0·0010	+0·00028	100	0·28	—	0·55
6.	0·0852	0·0866	+0·0014	+0·00039	100	0·28	—	0·55
7.	0·0852	0·0847	−0·0005	−0·00014	200	0·28	20	0·55
8.	0·0852	0·0830	−0·0022	−0·00062	200	0·28	20	0·55
9.	0·0852	0·0811	−0·0041	−0·00115	300	0·28	60	0·55
				B.				
10.	0·8111	0·8114	+0·0003	+0·00008	150,100	1·68	—,—	3·3
11.	0·8615	0·8613	−0·0002	−0·00006	150,100	1·68	—,—	3·3
12.	0·8615	0·8578	−0·0037	−0·00103	200,100	1·68	—,20	3·3
13.	0·8615	0·8487	−0·0128	−0·00358	200,100	1·68	—,60	3·3
14.	0·0852	0·0857	+0·0003	+0·00008	100,100	0·28	—,—	0·55
15.	0·0852	0·0656	+0·0004	+0·00011	100,100	0·28	10,—	0·55
16.	0·0852	0·0853	+0·0001	+0·00003	150,100	0·28	10,10	0·55
17.	0·0852	0·0819	−0·0033	−0·00092	200,100	0·28	20,20	
				C.				
18.	0·8111	0·8071	−0·0040	−0·00112	120	1·4	—	2·75
19.	0·8111	0·8052	−0·0059	−0·00165	120	1·4	—	2·75

The Practical Determination of Magnesium and Phosphoric Acid.

In determining magnesium by the procedure in ordinary use, the tendency is strong—as is shown in Experiments 1 and 2 of Table IV.—toward high plus errors, and the error is due to the combined effects of excesses of the precipitant, the ammonium salt, and free ammonia. The Experiments 11 and 12 of B, Table III., show conclusively that such tendencies to error may be counteracted effectively by pouring off the supernatant liquid (through the filter to be used subsequently to collect the precipitate) as soon as the precipitate subsides, dissolving the phosphate in the least amount of hydrochloric acid, bringing it down again, after dilution, by a faint excess of ammonia, filtering (best, we think, on asbestos under pressure), washing with faintly ammoniacal water, and igniting as usual.

Many years ago (*Am. Journ. Sci.*, [3], v., 114) a method of precipitating the ammonium-magnesium phosphate was advocated by Professor Wolcott Gibbs, which consists essentially in boiling the solution of the magnesium salt with microcosmic salt and adding ammonia after cooling, and by which most exact analytical results were obtained. Our experience confirms completely that of Dr. Gibbs, and we desire to direct attention again to a procedure the advantage of which has, unfortunately, not been broadly known and accepted. Even in the presence of considerable amounts of ammonium chloride this process yields a phosphate of nearly ideal constitution if only the boiling be prolonged from three to five minutes. The greater part of the ammonium-magnesium phosphate—about 90 per cent—forms in this process before free ammonia is added, and the ammonium which enters the phosphate thus formed is derived from the microcosmic salt, which must become correspondingly acidic. Under these conditions, the tendency to form an insoluble ammonium-magnesium phosphate richer in ammonia and poorer in magnesia than the normal salt, does not develop. In the process of Dr. Gibbs, as well in the modified precipitation process in the cold, the use of the faintly ammoniacal solution and wash-water is sufficient and advantageous.

In the precipitation of a soluble phosphate by magnesia mixture, the tendency of the precipitant and that of the ammonium salt are antagonistic, so that the effect of the latter salt is somewhat masked, though manifest. This opposition of effects has been noted by Mahon (*Journ. Am. Chem. Soc.*, xx., 445), who, though regarding the actual attainment of an exact balance as uncertain, ventures the opinion that accurate results should be attainable by the careful relative adjustment of the proportions of the precipitant and ammonium salt. Mahon claims to get the best results by a very gradual addition of magnesia mixture to the ammoniacal solution of the phosphate containing about 16 per cent of ammonium chloride, strong ammonia being added subsequently. From our observations, however, recorded in Section C of Table VI., it appears that the method of introducing the magnesia mixture gradually into the ammoniacal phosphate (taken in quantity sufficiently large to give unmistakable indications) produces a precipitate deficient in magnesium, and so leads to errors of deficiency in the phosphorus indicated. The use of strong ammonia, moreover, we have shown to be both unnecessary and disadvantageous. Our experiments go to show that good results may be expected when the solution of the phosphate containing a moderate excess of the magnesium salt and not more than 5 to 10 per cent of ammonium chloride is precipitated by making it slightly ammoniacal—the precipitate being washed in slightly ammoniacal wash-water. In general, however, and especially when more ammonium chloride than this proportion, or more magnesium salt than twice the amount theoretically necessary, is present, it is safer to decant the supernatant liquid from the precipitate (through the filter to be used subsequently to hold the phosphate), to dissolve the precipitate in a little hydrochloric acid and re-precipitate by dilute ammonia, washing with faintly ammoniacal wash-water.

Relative Speeds of Saponification of the Ethers of the Higher Homologues of Oxalic Acid.—E. Hjelt.—The author has found that the speed of saponification diminishes regularly as the carboxyls are further one from the other; while, on the contrary, the degree of dissociation of the second atom of hydrogen gradually increases.—*Berichte der Deutsch. Chem. Gesell.*

PRESIDENTIAL ADDRESS TO THE IRON AND STEEL INSTITUTE.

By Professor Sir W. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S.

(Continued from p. 249).

1846. It is perhaps natural that in the rest of the first half of the century the most noteworthy feature seems to be the renewed attention devoted to the investigation of the nature of oxidation and reduction. As the investigations, which were of great importance, were mainly conducted on the Continent, I must reluctantly leave their consideration until a future meeting. In the blast-furnace there was evidently a kind of tidal ebb and flow in the relations of carbon and of oxygen, resulting sometimes in reduction, and at others in oxidation or carburisation; but the changes were all capable of more or less simple expression if viewed either from the atomic or the dynamic standpoint. As the furnaces grew in dimensions, their flaming tops threw a lurid glare over the country, and, "like the dying sunset kindled through a cleft," revealed the magnitude of the problems involved in blast-furnace practice, which were seen to be disproportionate to their apparent simplicity.

As regards the study of the nature of the ascending gaseous column, I may anticipate the remarks I shall have to make next year by pointing out that the labours of the illustrious chemist Bunsen were shared by the late Lord Playfair, and that a joint communication of theirs was published in the Report of the British Association for the year 1846.

In the first half of the century efforts were directed mainly to obtaining a material,—cast-iron containing some 3½ per cent of carbon, and fusible at a temperature readily attained in the blast-furnace. In the second half of the century, while efforts to obtain this fusible material were increased, attention was also directed to removing the carbon, and obtaining a product which had a melting-point of 400° C. (720° F.) higher than cast-iron. This product was either cast directly into ingot moulds or re-carburised to the extent necessary to constitute the various gradations of steel. Sheffield hardly knew steel except as a material to be used for the manufacture of cutlery, for which she had been famous since the time of Chaucer.

It is characteristic of our British methods that special circumstances and needs, mainly arising in connection with the development of the steam-engine and railways, revealed the broad principles by which the production of iron must be governed. It was natural, therefore, as time went on, that in the work of successive inventors the guidance of scientific principles became progressively evident as ill-directed efforts were gradually replaced by the results of systematic experiments.

1850-51. The second half of the century began with events of strange importance. The Great Exhibition revealed our industrial strength to all nations. The official reporter of the Metallurgical group states that 2,250,000 tons of pig-iron were annually produced in this country, and that its estimated value was £5,400,000. The annual production had risen in fifty years from 200,000 tons to over two and a quarter millions. Sheffield produced at the opening of the century 35,000 tons of steel, of which 18,000 tons were cast-steel. Messrs. Turton exhibited a single ingot of steel weighing 2688 lbs., but Krupp showed an ingot of double the weight, for our country was only preparing for the great change which was so soon to enable it to lead the steel manufacture of the world.

A noteworthy feature of the Exhibition was the collection of iron ores of this country exhibited by Mr. Blackwell, who subsequently, and most generously, provided a large sum towards the cost of their analysis. With reference to this collection, the reporter points out that in this country "the ores are not carried far, except where there is great facility for transport." This is noteworthy, as before the century was much older an important supply of ore was brought from Spain, and in the near future we may even seek a supply for British furnaces from distant parts of our own Empire.

The year 1851 was, moreover, an important one for metallurgy in this country, as it saw, by the wisdom of H.R.H. the Prince Consort, the establishment of the Institution which developed into the Royal School of Mines. If the projected scheme of instruction had been fully carried out, the establishment of a general system of technical instruction, which the pressure of necessity is slowly forcing upon us, would have been anticipated by forty years.

In the year of the Great Exhibition the blast-furnaces seldom exceeded 50 feet in height, and it was not until 1864 that Mr. John Vaughan erected a furnace 75 feet high, with remarkable results as regards increased output; since then the gigantic furnaces of the Cleveland district have become common.

1856. The year 1856 will be ever memorable in the metallurgical annals of our nation as that in which Bessemer gave the description of his process to the world at the Cheltenham Meeting of the British Association. As regards the process itself, we have too lately lost our great countryman, and many of us are too familiar with the details of his labours to be able either to fully estimate its value or to realise the wonder of its results. Let us try to think of the Bessemer process as I believe those at the end of the twentieth century will, whose views range over a wider perspective than we can command. The economic aspect of the question will naturally strike the metallurgists of the twentieth century. They will see that in 1855 the make of steel in Great Britain did not exceed 50,000 tons, and the cost of the steel produced sometimes reached £75 a ton. They will see that thirty years after the publication of Bessemer's paper the production of Bessemer steel rose to 1,570,000 tons, and that ship plates were sold at £6 10s. a ton. It will be noted that before the century closed, the maximum production of Bessemer steel in this country in one year reached 2,140,000 tons. The scientific aspect of the process will, however, excite their widespread interest, for before the end of the twentieth century metallurgy will be taught in our older universities. It will be seen that, notwithstanding the title of Bessemer's Cheltenham paper, he recognised and insisted on the fact that the intense heat was engendered by the combustion of the elements within the fluid bath. It will be noted in what close relation the purely scientific work of Thomas Andrews of Belfast, on the heat of combination, stands to that of Bessemer, and that another instance is presented of the dependence of industrial work on pure investigation. Bessemer's proposal to employ a mixture of steam and air will not be ridiculed as it has been, for speculation will be rife as to whether he did not hope that the liberated hydrogen might remove sulphur and phosphorus, notwithstanding the feebly exothermic result of the ensuing combination, and in spite of the cooling effect of water-vapour. In view of the fact that endothermic combinations take place at a high temperature, the possible action of hydrogen as a decarburiser will be dwelt upon. Prof. Noel Hartley's papers upon the Thermo-chemistry of the Bessemer Process will be read with much interest. Surprise will, however, be widely felt that physicists generally of the last half of the nineteenth century did not see in the lovely flames of lilac, amethyst, gold, and russet, or in the "stars suspended in a flying sphere of turbulent light" which come from the converter, an appeal to fully investigate their cause and to study the dynamic problems presented by the intense heat engendered. Why was not the destination ascertained of the 1000 cubic feet of argon which accompanies the air passing through the metal during an ordinary Bessemer 10-ton blow? Why were not more strenuous efforts made to ascertain the

effect of the temperature of the bath on the nature of the metal?

It will be felt that, as the eighteenth century had closed with a clear statement as to the true nature of oxidation, the nineteenth century had seen its magnificent application in the Bessemer process.

As regards the work of Mushet, future generations will, I believe, desire to add nothing to the words of the President of this Institution, who, in 1875, had the pleasure of awarding the Bessemer Medal to him. Mr. Menelaus then said "that the application of spiegeleisen . . . was one of the most elegant, as it certainly was one of the most useful, inventions ever made in the whole history of metallurgy."

1861. Attention must now be directed to the great process for the production of steel which involved the use of the "open hearth."

Sir William Siemens's life was one long and ultimately brilliantly successful effort to apply the kinetic theory of gases and the dynamical theory of heat to industrial practice. He was eminently a practical worker; but the depth and accuracy of his scientific knowledge gives him a place near that of all the great atomists from the time of Lucretius to that of our own countrymen, Graham, Joule, Clerk Maxwell, and Kelvin. In many of Siemens's papers, theory and practice are closely blended. In viewing the results of his labours, it will be seen in future ages that confidence in the trustworthy character of steel was finally established by experiments on metal produced in the regenerative furnace of Siemens. Looking back, it is astonishing with what difficulties the use of steel for structural purposes was beset. In 1859 Sir John Hawkshaw was not permitted by the regulations of the Board of Trade to employ steel in the construction of the Charing Cross bridge. Time will not permit me to indicate the efforts which were made to induce the Board of Trade to remove the serious hindrances to the use of steel, which had "rendered the construction of the projected bridge over the Firth of Forth practically impossible." These efforts were not successful until 1877, when a Committee, consisting of Sir John Hawkshaw, Colonel Yolland, and Mr. W. H. Barlow, were able to recommend that the employment of steel in engineering structures should be authorised by the Board of Trade. The steel employed was to be "cast steel, or steel made by some process of fusion, subsequently rolled or hammered"; one condition of such recommendation being that "the greatest load which can be brought upon the bridge or structure, added to the weight of the superstructure, should not produce a greater strain in any part than 6½ tons per square inch."

As regards the use of steel for shipbuilding purposes, in this same year, 1875, Sir Nathaniel Barnaby asked, "What are our prospects of obtaining a material which we can use without such delicate manipulation and so much fear and trembling?" He partly answered his own question, four years later, when he quoted experimental evidence as to "the recent successes" of open-hearth steel. In 1890 he completed the case by pointing out that naval architects now "have a perfectly regular material, stronger and more ductile than iron," and he speaks of "our lasting debt of gratitude for the birth and training of that true prince, William Siemens." It is hardly necessary to point out that the country owes the excellent materials used in naval architecture mainly to the productions of the regenerative furnace.

In connection with the production of mild steel, the addition of ferro-manganese to the decarburised bath proved to be most effective. We can hardly over-estimate our indebtedness to those whose perseverance ensured the adoption of mild steel for maritime and other purposes. "Looked at from the standpoint of to-day, when thousands of tons of such steel are made weekly without serious anxiety or trouble, it is scarcely possible to realise the anxieties and difficulties of the days when the manufacture of open-hearth steel was being perfected." To no one is our debt greater than to our Vice-President, Mr. James Riley, who bore a large share of the anxieties of the early days, and whose words are those I have just quoted.

With regard to the great modifications which have been effected in the Bessemer and open-hearth processes, reference must be made to that ample source of information, our *Journal*. It must also be consulted for the history of the appliances for heating the blast with which the names of Cowper and of Whitwell will always be specially connected.

In speaking of Bessemer and Siemens I have been obliged to depart somewhat from strict chronological order. I must now resume it at the year 1865.

1865. Sir Joseph Whitworth patented on November 24, 1865, a process for submitting liquid steel to heavy pressure, at the critical juncture when the metal is passing from the fluid to the semi-fluid state, to prevent any part of the casting from becoming hollow or unsound.

1866. In the year 1866 Graham's first paper on the occlusion of gases by metals was published in the *Philosophical Transactions*. Its results have been far-reaching, and will always be regarded as one of the metallurgical triumphs of the century.

1869. In the year 1869 our Institute was founded. In view of certain aspects of the treatment which inventors had previously received from their industrial brethren and from the country, it will be evident that the time for its formation had fully come. Taking instances almost at random, I may remind you that Dud Dudley was, as he says, "with lawsuits and riots wearied and disabled" in the seventeenth century, and that Henry Cort was neglected and oppressed in the eighteenth. The great invention of iron bottoms in the puddling-furnace made by Rogers was received with ridicule, and he died in poverty. Popular tradition of Sheffield indicates that possession was obtained of Huntsman's secret "by the heartless trick of a rival." Neilson, though he warmly acknowledges the support he received from certain iron-masters, was treated with singular meanness by others. Heath fought single-handed for fifteen years "against a common purse, the accumulation of the wealth which he had created." Even Bessemer's early statements were received with incredulity and contempt. With the formation of our Institute all this is changed: men place the results of their work and experience freely at the disposal of their brethren, and each fresh advance meets with appreciative consideration. "Vigorous moderateness," wrote the late Walter Bagehot, "is the rule of a polity which works by discussion. . . . It was government by discussion that broke the bond of ages and set free the originality of mankind."

1869-71. The history of our industry since the formation of this Institute is epitomised by the labours of those who have hitherto occupied the Presidential chair. The Duke of Devonshire, K.G., our first President, worthily sustained the honour of the name of Cavendish, one of the most illustrious in the scientific annals of our country, and the connection of the Duke with the iron industry of Barrow is an incident of the first importance in our industrial records. He highly appreciated the importance of science in relation to the progress of the nation; and the Report of the Royal Commission on Scientific Instruction and the Advancement of Science, of which he was President, contributed in no small degree to the awakening of public attention to the subject. His noble foundation of the Cavendish Laboratory at the University of Cambridge stimulated research on lines closely connected with this Institute, as the work of Clerk Maxwell, of Rayleigh, of J. J. Thomson, of Ewing, and of Heycock and Neville, abundantly testify. It is certain that the main efforts of his life were directed to developing the resources and improving the condition of the people. Neither rank, wealth, nor intellectual gifts had power to affect the simplicity of his character or to lessen the deep sense of duty which controlled all his actions.

1871-73. The life-work of our second President, Sir Henry Bessemer, has already been dealt with, and the lesson it teaches is how vastly important the labours of one man may be to a nation. In these days the facilities for work are much greater than they were, and results are obtained by an army of workers; but, as Stanley Jevons has pointed out, the influence of the individual genius is "not withering, but is growing with the extent of the material resources which are at his command." It was during the Presidency of Sir H. Bessemer that Snelus patented the use of basic lining for furnaces and crucibles, which was ultimately found to be so important in relation to the elimination of phosphorus from pig-iron.

1873-75. Sir Lowthian Bell embodies for us the progress in blast-furnace practice of at least the last half-century. It was under his Presidency that the first Continental meeting was held, the place chosen being Liége, Belgium's great metallurgical centre. He was the author of the first paper communicated to the Institute, choosing as a subject "The Development of Heat and its Appropriation in the Blast-Furnace." There is a passage in the Presidential Address of Dr. Percy, with reference to the work of Sir Lowthian Bell, which I may be permitted to quote. Dr. Percy said:—"His laborious, careful, and original investigations of scientific problems of the highest interest in the metallurgy of iron and steel, must be so well known to this audience that any comment upon them from me would be superfluous, if not presumptuous." If Dr. Percy, the metallurgical historian of the age, thus shrank in 1885 from the attempt to give adequate expression to the value of Sir Lowthian's work, it would be impertinent in me to say more than that the fourteen years which have passed since Dr. Percy wrote have only served to bring into greater prominence Sir Lowthian's unswerving devotion to the solution of those problems he has so patiently studied.

1875-77. Attempts to improve the ancient operation of puddling by the aid of mechanical appliances, received their fullest development under the guidance of William Menelaus. The great usefulness of his career may perhaps be well indicated by the statement that he was among the first to be convinced of the vast superiority of steel to puddled iron, and urged its adoption with singular foresight and vigour. His position as manager of Dowlais Works gave great force to his advocacy. By lending his great mechanical resources and power of organisation to scientific research, he brought about some of the greatest improvements that were ever effected in the iron and steel industries. He associated himself, moreover, with Edward Riley, who, as an analytical chemist, subsequently made a distinguished name.

1877-79. The work of Sir William Siemens has already been dealt with as fully as time will permit. I will, therefore, only quote the public tribute to his memory which was offered at the time of his death in 1883:—"The nation at large has lost a faithful servant, chief among those who live only to better the life of their fellow-men by subduing the forces of Nature to their use. Looking back along the line of England's scientific worthies, there are few who have served the people better than this, her adopted son—few, if any, whose life's record will show so long a list of useful labours."

1879-81. Edward Williams shares with Menelaus the unique distinction of having been the first to appreciate the great importance of Bessemer's discovery, and within three days after the publication of Bessemer's paper at the British Association he erected at the Dowlais Works a small fixed converter, had blown pig-iron, and had rolled the product into bars, "to the great astonishment of all concerned." His vigorous address as President of this Institute was remarkable for the then prophetic expression of belief, that the day was "at hand when either by a Bessemer converter or by the open-hearth . . . there will be produced with absolute certainty, with comparatively light labour, and (he hoped) with fair profit to all concerned, every kind, variation, and quality of the metal iron which we rudely designate steel and wrought iron." He also made a striking appeal to educated intellectual young men who "hung listlessly" about the professions "to break through the absurd old prejudice against seemingly rough work, and come over to the healthy business of iron and steel-making, in which they might render the world good service."

1881-83. Josiah Timmis Smith, in his Presidential Address, gave a remarkable retrospect of the period which had elapsed since the foundation of the Institute. He showed that, comparing the year 1880 with the year 1869, 2¼ millions more tons of iron had been made with the same amount of fuel, or we had, in fact, economised our fuel supplies to the extent of 10,000,000 tons. He gives a masterly summary of the progress in our industries, and eloquently pleaded that chemistry had proved its claims to be regarded as the handmaid of the iron manufacturer, and had given our metallurgical art a place in relation to the exact sciences which it could never otherwise have occupied. He also urged with great force that our Institute had broken down the spirit of exclusiveness and prejudice, that is usually the most rampant where knowledge is most wanting.

1883-85. To Sir Bernhard Samuelson is due the credit of being the first to succeed in convincing the House of Commons of the national importance of Technical Education in its widest sense, and to induce it to grant a Select Committee to inquire into the provisions for giving instruction in theoretical and applied science to the industrial classes. I wish I knew which of his wise and careful utterances he would like me to quote. Left to my own choice, I reject reference to his elaborate array of statistics, and select the following brief passage from his Presidential Address:—"It is to the further development of the world's railways that we must mainly look in the future as in the past for the support of our trade." Bearing in mind what is happening in Egypt, in South Africa, in China, and on the frontiers of our Indian Empire, the vast importance of railways, to which Sir Bernhard refers, cannot be doubted. Hence the engineer, considered as a pioneer, is absolutely dependent for steel rails and for the material for the construction of bridges on the metallurgist, whose work is the real foundation of progress. One other sentence, which is typical of the whole tenor of his life's work, may be quoted:—"It is in the mutual co-operation (in a scientific spirit) of every grade in our great craft that we may build up the hope, nay, that we may cherish the certain expectation, of placing it on even a higher eminence than that which it has already attained.

(To be continued).

Royal Institution. — Forthcoming Centenary Celebrations.—In the month of June the Royal Institution of Great Britain will complete one hundred years of its existence, the first meeting of its Members in the building in Albemarle Street having been held on the 5th June, 1799. The Managers have decided that this event, so interesting and memorable in the life of the Institution, and in the history of science in this country, should be duly celebrated. They have, therefore, arranged for the delivery of two Commemoration Lectures. The first of these Lectures will be delivered at 3 o'clock on Tuesday, the 6th of June, by Professor Lord Rayleigh, when His Royal Highness the Prince of Wales, Vice-Patron of the Institution, will preside and receive the Honorary Members; the second of these Lectures will be delivered at 9 o'clock on Wednesday evening, the 7th of June, by Professor Dewar, when His Grace the Duke of Northumberland, President of the Institution, will preside. It is further announced that the Lord Mayor has, in the kindest manner, consented to give a reception to the Members, Foreign Guests, and Representative Men at the Mansion House, on the evening of Tuesday, the 6th of June.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, May 18th, 1899.

Professor THORPE, F.R.S., President, in the Chair.

MESSRS. H. H. Bowles, F. S. Young, and R. Haliburton Adie were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George Dekeyne Atkinson, care of Crowley and Co., The Brewery, Alton, Hants; James Connah, Geralton, Carlton Road, Sidcup; Robert McClumpha, 372, Westgate Road, Newcastle-on-Tyne; Eskricke Sidney Phillips, Christ's College, Cambridge; John William Shepherd, 48, Ovington Street, S.W.; Charles Simmonds, 17, Ruvigny Gardens, Putney, S.W.

Of the following papers those marked * were read:—

*71. "*Corydaline.*" Part VI. By JAMES J. DOBBIE and ALEXANDER LAUDER.

In this paper the authors give the results of the investigation of *corydaldine*, $C_9H_7NO(OCH_3)_2$, one of the substances obtained by the oxidation of corydaline by means of potassium permanganate (*Trans.*, 1894, lxv., 57). By employing a smaller proportion of permanganate and using it at the ordinary temperature, a larger yield was obtained than by the method previously described.

Corydaldine readily dissolves in water, melts at 175°, and contains two methoxyl groups. Dissolved in hydrochloric acid and treated with sodium nitrite at 0°, a yellow nitroso-derivative is obtained (m. p. 185°), which is very insoluble in hot and cold water. When this nitroso-derivative is gently warmed with a solution of sodium hydrate, nitrogen is evolved, and on addition of hydrochloric acid to the solution a new substance, melting at 138—139°, is obtained, which is the anhydride of a monobasic acid. Its formula is $C_{11}H_{12}O_4$; it is difficultly soluble in cold but readily in boiling water, from which it crystallises well on cooling. Treatment with hydrogen iodide proves that it contains two methoxyl groups, and oxidation with permanganate at 100° converts it into metahemipinic acid. Heated with hydrochloric acid at 150°, a phenolic derivative (m. p. 232°) is obtained, which shows all the reactions of ω-hydroxyethylcatecholcarboxylic anhydride obtained by Perkin from berberine (*Trans.*, 1890, lvii., 1028). The authors therefore conclude that *corydaldine* only differs from ω-amidoethylpiperonylcarboxylic anhydride in having two methoxyl groups instead of the piperonyl group, and that it is closely related to oxy-hydrastinine.

Corydaline is thus proved to be closely related to berberine, hydrastine, narcotine, and papaverine, in common with which it contains an isoquinoline nucleus. When the alkaloid is oxidised at 100° by means of potassium permanganate, the chief product is a mixture of hemipinic and metahemipinic acids.

The substance previously described under the name of corydalineic acid (*Trans.*, 1894, lxv., 57) is found to be an acid ammonium salt of metahemipinic acid, having the formula $C_{10}H_{10}O_6,C_{10}H_9O_6(NH_4),3H_2O$.

*72. "*Oxidation of Furfural by Hydrogen Peroxide.*" By C. F. CROSS, E. J. BEVAN, and T. HEIBERG.

The results described in this paper are obtained by interaction of the aldehyde and peroxide in dilute aqueous solution (2—4 per cent furfural) at 40° in presence of iron salts in small quantity. The peroxide is added until the characteristic reaction of the aldehyde with aniline acetate is no longer obtainable, the quantity of peroxide required being 2 to 3 molecules per molecule of furfural.

The main product of oxidation is recognised by its reactions with phenylhydrazine (formation of hydrazone), and with phloroglucinol and hydrochloric acid (deep red-violet colouration followed by precipitation of the colouring matter) to be a furfural derivative. Analysis of the hydrazone shows it to be the hydrazine derivative of a *hydroxyfurfural*. Along with this main product is an acid, which is easily separated as a barium salt insoluble in acetic acid. Analysis of the barium and lead salts show the acid to be the corresponding *hydroxypyromucic* acid.

The substitution of hydroxyl for hydrogen in the furfurane nucleus agrees with the results of previous investigations as to the mode of action of the peroxide; but, as a further confirmation, its action on benzene under conditions similar to those in the above described experiments has been so far studied as to prove the formation of a considerable quantity of phenol. The furfural-phenol corresponds to an oxybenzaldehyde; reasons are given for regarding the OH and CHO-groups as occupying the 1 : 2-positions. It is noteworthy that, as in the case of the normal saturated "carbohydrates," the CHO-group is but slowly attacked by the peroxide relatively to a CH-group.

The further action of the peroxide is destructive in character, the furfurane ring being being broken down, the chief product being formic acid, along with some acetic and oxalic acids. The intermediate products appear from their reactions to be hydroxyketonic acids. The formation of methylated compounds is probably a secondary result of the decomposition; from the products of the original reaction, iodoform is obtainable in some quantity, and the amounts have been estimated.

Special interest attaches to the hydroxyfurfural which has been thus obtained. Its reactions with phloroglucinol andwith resorcinol in presence of HCl are similar to those of the lignocelluloses. These colours may be developed on a pure cellulose cloth or paper for comparative study. It is then seen that the brilliant colours of the original products—blue with resorcinol, violet with phloroglucinol, give place to "flattened" shades, grey and brown respectively, on washing with ordinary water.

By means of these reactions, it is now shown (1) that a furfural-phenol is a constituent of the lignocelluloses; (2) that the colour reactions of these "natural" products with the hydroxybenzenes are due to the presence of such compounds; (3) that the equally characteristic reactions of the lignocelluloses with aniline salts are reactions with a second constituent group, *e.g.*, the keto-R-hexene complex.

A furfural-phenol being a normal product of the condensation processes accompanying lignification, it is probably also a product of the action of the condensing acids used in estimations of furfural. It appears, therefore, that the furfural actually isolated does not necessarily represent the entire production of furfurane derivatives; and these observations supply the basis for a further differentiation of the complex group of furfural-yielding plant constituents or furfuroids.

DISCUSSION.

Mr. F. S. YOUNG said that, as the result of some preliminary experiments, he had found that, although hydrogen peroxide by itself attacks benzene only very slowly, an extremely energetic reaction takes place in the presence of ferrous salts. A complete examination of the products of the reaction has still to be made; but he had proved that a considerable quantity of phenol is formed.

In two preliminary experiments, in which 1 molecule and 2 molecules of hydrogen peroxide were used for 1 molecule of benzene, the yield of phenol was 10 per cent and 20 per cent respectively; and it is possible that this yield may be increased when the most favourable conditions for its formation have been determined. Pyrocatechol was also obtained as a product of the reaction.

Mr. FENTON said that the results obtained by Messrs. Cross and Young with furfural and benzene, together with those which had been observed by himself and others in the case of phenol, appeared to establish a third typical reaction of hydrogen peroxide in presence of iron, —namely, the replacement of hydrogen by hydroxyl.

With reference to Mr. Cross's suggested explanation of the mechanism of the reaction, he did not think that it was applicable to the cases which he (Mr. Fenton) had studied, since other oxidising agents might be substituted for the hydrogen peroxide.

Mr. CROSS, in reply, said with regard to the mechanism of the action of hydrogen peroxide, that although the tendency of the peroxide to split into hydrogen and oxygen might not be suggested by the interactions with inorganic compounds, yet its behaviour with carbon compounds, especially those which are unsaturated, might furnish evidence of such intermediate phases as would disappear in the final stages of the reaction.

*73. "*Note on the Reactions between Sulphuric Acid and the Elements.*" By R. H. ADIE.

The publication of a paper by M. Berthelot on the action of sulphuric acid on metals (*Ann. Chim. Phys.*, 1898, [vii.], xiv., clxxvi., 176—204), leads the author to publish the results of some experiments which he performed some years ago. The results obtained by Berthelot in the case of zinc confirm those of Muir and the author (*Trans.*, 1888, liii., 47, and, in the case of copper, those of Pickering (*Trans.*, 1878, xxxiii., 112). In the following table, the temperatures of decomposition of sulphuric acid by the easily obtainable elements are given, these being grouped according to the periodic system.

It appears possible, even at this stage, to draw a few conclusions:—

(i.) Sulphuric acid is decomposed by most elements with the formation of sulphur dioxide and hydrogen. Sulphuretted hydrogen only appears as a special impurity in a few cases.

(ii.) In any group of elements the decomposition temperature becomes lower as the atomic weight of the element increases.

(iii.) Copper, nickel, and palladium, all form black sulphides, and also all give compounds with ammonia.

(iv.) In the case of zinc, a pure specimen (kindly given by Professor Ramsay) caused the temperature of decomposition to rise to 250°. With this specimen, no hydrogen sulphide was evolved up to the boiling-point of the acid. This suggests the unsuitability of ordinary zinc for further work.

Element.	SO_2 appears.	H_2S appears.	Notes.
Hydrogen	170°	None	Gas prepared from Zn and HCl washed and dried with H_2SO_4.
Copper	Begins 110—115° Continuous 120°	None	Cu_2S formed.
Silver	175°	None	Gas evolved at 150°.
Magnesium	215°	Trace	
Zinc	250°	None	SO_2 evolved as soon as reaction starts.
Cadmium	205°	Trace?	
Mercury	120°	None	Gas given off at 110°.
Aluminium	235°	None	No bubbles of SO_2.
Carbon	188°	None	
Tin	145°	None	S formed.
Lead	140°	None	
Thallium	Below 20°	Below 20°	Formed at once at ordinary temperature. Brown solid formed.
Arsenic	110°	None	No AsH_3.
Antimony	90—95°	None	
Bismuth	90°	None	Gas evolved at once.
Sulphur	200°	None	Melts at 220°. No bubbles till 230°.
Selenium	170°	None	
Molybdenum	135°	None	Gas begins at 115°. Green solid formed.
Tungsten	175°	None	
Manganese	155°	None	Gas evolved at 120°.
Iodine	—	—	Passes over at 92°. No action before.
Iron	220°	None	Gas evolved at 170°.
Nickel	145°	None	Black solid formed.
Cobalt	240°	None	
Palladium	200°	None	Reaction not vigorous. Blackens from formation of sulphide.
Platinum	None	None	

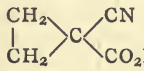
The author intends to make a fuller investigation of some of the more definite reactions.

74. "*On the Action of Ethylene Dibromide and of Trimethylene Dibromide on the Sodium Derivative of Ethylic Cyanacetate.*" By H. C. HAROLD CARPENTER and WILLIAM H. PERKIN, jun.

One of the great difficulties in investigating the derivatives of trimethylene is the fact that the condensation of ethylene bromide with the sodium compounds of ethyl malonate and ethyl acetoacetate gives only a very small yield of trimethylene compounds (*Trans.*, 1885, xlvii., 808); and again, in investigating the formation of tetramethylene compounds by the action of trimethylene bromide on the sodium derivative of ethyl malonate, the best yield of ethyl tetramethylenedicarboxylate (1,1) obtained was only 33 per cent (*Trans.*, 1887, li., 3).

It appeared to us possible that the yield of these closed-chain compounds might be considerably increased if ethyl cyanacetate was substituted for ethyl malonate and acetoacetate, and this has been found to be the case.

Ethyl trimethylenecyancarboxylate (1,1),—



of which 50—60 per cent is obtained by the action of ethylene bromide on the sodium derivative of ethyl cyanacetate, is a colourless mobile liquid boiling at 210—211° under 766 m.m. pressure, $\Delta\ 0°/4° = 1{\cdot}0783$. It dissolves gradually in aqueous ammonia (sp. gr. = 0·88) forming the amide, which crystallises in lustrous needles (m. p. 160°). Cold methyl alcoholic potash saponifies it instantly, with the production of the potassium salt of *trimethylenecyancarboxylic acid* (1,1). The acid is obtained in the form of long colourless prisms by the evaporation of its ethereal solution in a stream of dry air. It melts undecomposed at 148°. It is remarkable that all attempts to split off the carboxyl group and prepare cyantrimethylene, (i.) by distilling the acid, (ii.) by heating it in sealed tubes with a small quantity of water, (iii.) by heating the silver salt, have failed. Recently, however, this substance has been prepared by L. Henry, who distilled γ-chlorbutyronitrile repeatedly over solid potash and obtained it in the form

of a colourless liquid of pleasant odour. B. p. = 135°, Δ 16°=0·911 (*Bull. Acad. Roy. Belgique*, 1898, [3], xxxvi., 34; 1899, [3], xxxvii., 17—22).

The silver salt is a very characteristic substance. It is soluble in water, and crystallises from its aqueous solution in lustrous prisms. The conversion of the trimethylenecyancarboxylic acid into trimethylenedicarboxylic acid is best effected by boiling with aqueous potash. From the latter acid, its characteristic derivative, bromethylmalonic acid (m. p. 116°) was prepared by the action of aqueous hydrobromic acid (sp. gr. = 1·83).

The condensation of ethylene bromide with the sodium derivative of ethyl cyanacetate yields, besides the trimethylene derivative, two crystalline substances, the one melting at 119°, the other at 95—96°, according as the reaction is made to take place under pressure in soda-water bottles or at ordinary pressures. These substances have been analysed, but their constitutions have not yet been discovered.

Ethyl tetramethylenecyancarboxylate (1,1),—

$$\begin{matrix} CH_2—CH_2 \\ | \quad\quad | \\ CH_2—C(CN).CO_2Et \end{matrix},$$

is obtained to the extent of 60—70 per cent by the action of trimethylene bromide on the sodium derivative of ethyl-cyanacetate. It is a colourless liquid boiling at 213—214° under 766 m.m. pressure, Δ 0°/4° = 1·0633. It dissolves in aqueous ammonia (sp. gr. = 0·88), but the resulting amide is easily soluble and does not crystallise out. Cold methyl alcoholic potash saponifies it at once, forming the potassium salt of *tetramethylenecyancarboxylic acid* (1,1). The free acid is purified by crystallisation from carbon disulphide containing a small quantity of ether, and is thus obtained in long silky needles, which have the remarkably low melting-point 69—70°. By careful heating they may be sublimed unchanged. The silver salt is completely analogous to that of the corresponding trimethylene acid. Boiling aqueous potash hydrolyses the cyanogen group, and the product is tetramethylenedicarboxylic acid (1,1), which melts at 157°. The characteristic lead salt was prepared and analysed. The by-product in the preparation of the ethyl tetramethylenecyancarboxylate is an oil. The investigation of this substance is in progress.

75. "*The Maximum Vapour-pressure of Camphor.*" By R. W. Allen, M.A.

By the two methods which he employed in determining the vapour-pressures of naphthalene (*Proc.*, 1899, xv., 122), the author has determined the maximum pressures of camphor vapour from 0—80°. The results obtained by these methods agree throughout, but differ very notably from those obtained by Ramsay and Young (*Phil. Trans.*, 1884, clxxv., 45).

PHYSICAL SOCIETY.

Ordinary Meeting, May 26th, 1899.

Mr. T. H. Blakesley, Vice-President, in the Chair.

A paper by Prof. S. Young and Mr. Rose-Innes, on "*The Thermal Properties of Normal Pentane*," Part 2, was read by Mr. Rose-Innes.

In the first paper on this subject, read before the Physical Society last December, it was shown that the relations existing between the volume temperature and pressure of normal pentane could be closely represented by the equation—

$$p = \frac{RT}{v}\left\{1 + \frac{e}{v + k - gv^{-2}}\right\} - \frac{l}{v(v+k)}.$$

This formula was first used in connection with isopentane, and it has been shown that the values of R and *l/e* are the same for the two isomers. The authors find that, if *l* and *e* be taken separately equal to each other, and if the constants *k* and *g* be calculated from experiments on normal pentane, errors of 2 per cent occur between the calculated and experimental results. This point has been investigated both algebraically and graphically, and the supposition that these constants are separately equal has been thought incorrect. Taking the values of R, *l/e*, and *g* as being the same in the two pentanes, the constants *l* and *k* have been determined, and by this means the relations between volume temperature and pressure have been represented by the formula to within 1 per cent. The authors conclude that the difference in pressure of two isomeric substances at a given volume and temperature is of the same order as the deviation from Boyle's Law, and involves the second power of the density.

Mr. Rose-Innes said the formula proposed was not an absolute solution of the problem, although it was the best of a large number which had been tried. It has been applied with success to Andrews's experiments on carbonic acid, and to experiments which have been made upon ether and hexane. In the latter case the range in volume was too small to afford a rigorous test of the value of the formula. The range in volume in isopentane was from 400·0 to 3·4, in normal pentane from 300 to 3·4, and in ether from 350 to 3·4. The temperature varied in different experiments from 40° C. to 280° C. Objections have been raised to the formula on account of the number of constants it contains, and its complexity. Mr. Rose-Innes pointed out that it was necessary to have a complex formula, as they were not dealing with a simple problem, but with the results of experiments which went so far below the critical temperature that the volume occupied was only 3·4 times as great as the space which would have been occupied by the molecules at their closest packing. The reader of the paper compared the proposed formula with formulæ of Clausius, Sutherland, and Tait, containing 4, 4, and 6 constants respectively, and, finally, with the original equation of Van der Waals applied to experimental results by Amagat. It was shown that the agreement was much closer and the range greater.

Prof. Callendar expressed his interest in the wide applicability of the author's formula, and asked if any theoretical significance could be assigned to the various constants which appeared.

Mr. Rose-Innes said the R of their formula was the R of the perfect gas equation, and that the *l* and *e* corresponded respectively to the β and α of the ordinary Van der Waals expression. So far as he knew the *k* and *g* were meaningless.

A paper "*On the Distribution of Magnetic Induction in a Long Iron Bar*," by Mr. C. G. Lamb, was postponed until the next meeting.

CORRESPONDENCE.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

Sir,—In my letter in last week's Chemical News an error has crept into the equation showing the number of c.c. of English test-acid required to neutralise 4·1 grms. of caustic soda. Instead of "$\frac{4·1 \times 100}{4·0} = 100·61$," it should, of course, be "$\frac{4·1 \times 100}{4·075} = 100·61$."—I am, &c.,

John Pattinson.

75, The Side, Newcastle-upon-Tyne,
May 30, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 18, May 1, 1899.

A Double Carbonate of Potassium and Peroxide of Cerium.—André Job.—In a former paper, the author has shown that it is possible to peroxidise cerium in aqueous solution, and to maintain it in the peroxidised state in a stable form. Perceric solutions of potassium carbonate, prepared by peroxide of hydrogen, were so kept for several months. The present paper contains an account of the method of isolating the contained perceric salt. The solution is slowly evaporated at the ordinary temperature until crystals of an intense blood-red are deposited, which attain the length of about half a centimetre. These crystals on examination are found to belong to the triclinic system. This fact, in itself, is enough to show the presence of a new chemical compound, since none of the known substances obtained from the same solution crystallise in this system. The author has prepared these crystals in a state of purity, analysis showing them to be a well-defined double carbonate of potassium and peroxide of cerium having the formula $(CO_3)_3Ce_2O_3.4CO_3K_2.12H_2O$.

Supposed Fluorine contained in certain Mineral Waters. — F. Parmentier. — Fluorine or its compounds has been believed to be present in the waters of Mont Dore and Saint Honoré les-Bains, by the fact that after a time the glasses in which the waters are served become opaque—having the appearance of being etched by hydrofluoric acid. The waters in question are very rich in silica, which is often deposited on the surface at the source; they contain also bicarbonates of the alkalis and alkaline earths. The author has examined them carefully, and finds no presence of fluorine compounds in the water, but proves that the etched appearance of the glass is due to a very adhesive deposit of silica, and not to a fluorine compound. In many analyses of the waters of Mont Dore, no trace of fluoride of calcium was found.

Oxidising Power of Alkaline Periodates. — E. Péchard. — The author's experiments show that the periodates in alkaline or neutral solution have an oxidising effect on methyl-orange which is not possessed by iodates under the same conditions. In acid solution there is the same difference: peroxide of hydrogen decomposing periodic acid, whilst it has no effect on iodic. To explain these facts it must be assumed that these salts have a different constitution from the iodates and also from the perchlorates, which latter salts give none of the reactions mentioned above. The periodates, and in particular the salt $NaIO_4$, is able to liberate oxygen with analogous properties to that of ozone, and further investigation of the action of this salt on potassium iodide, iodine being liberated, confirms this theory.

Displacement of Mercury by Hydrogen.— Albert Colson.— (*a*) The action of hydrogen on a uniformly pulverised mercury compound is proportional to the weight of the solid. (*b*) The rapidity of absorption of hydrogen gas is not proportional to the mass—that is to say, to the pressure. In slow reactions it appears to be proportional to the molecular distance, *i.e.*, to the cube-root of the pressure. The author proves the above two statements by experiment. He also investigates the action of hydrogen on mercuric and mercurous salts. At 100° hydrogen has no action on corrosive sublimate, but reduces mercuric sulphate and nitrate. Powdered and dried mercurous nitrate slowly evolves nitrogen dioxide in presence of hydrogen at 100°:—

$$(NO_3)_2Hg_2 + 4H = 2NO + 2HgO + 2H_2O.$$

Luminous Phenomena produced by the Action of certain Ammonium Salts on Fusing Potassium Nitrite.—D. Tommasi.— If a crystal of ammonium chloride is thrown into fusing potassium nitrite, the crystal assumes the form of a brilliant globule, which becomes incandescent, then burns and disappears with a feeble detonation. If sulphate of ammonium is used instead of the chloride, the luminous effect is more intense. Ammonium nitrate, in contact with fusing potassium nitrite, produces the most remarkable of the luminous phenomena. If nitrate is used in the state of crystalline powder, a series of phosphorescent spots are noticed on the surface of the bath of potassium nitrite, but if a crystal is used, it immediately forms an incandescent globule surrounded by a phosphorescent ring having a very rapid circular motion. After a few seconds it disappears, burning with a violet flame.

Morphine and its Salts.—Emile Leroy.—The author's experiments show that morphine precipitated by KOH or NH_3 is identical with morphine crystallised in the hydrated state. In fact, it is observed during the experiments that the evolution of heat is not instantaneous, but is produced during two or three minutes, which shows that morphine set free by an alkali undergoes a progressive transformation, which tends finally to the crystalline state.

Racemisation of Camphor.—A. Debierno.—Ordinary active camphor can be completely racemised without using the high temperature which was believed to be necessary. The author obtains this result by acting upon the molecular combination which forms camphor with aluminium chloride.

Tetramethylated Disymmetric Derivatives of Diamidodiphenylethane.—A. Trillat.—Disymmetric tetramethyldiamidodiphenylethane can be prepared by using, instead of pure acetic aldehyde, a mixture of alcohol and acetal, such as can be obtained by oxidising ethyl alcohol by potassium bichromate and dimethylaniline. The acetal decomposes, forming acetic aldehyde, which combines with the dimethylaniline—

$$CH_3.CH\lessdot^{C_2H_5O}_{C_2H_5O} + 2C_6H_5N(CH_3)_2 =$$
$$= CH_3.CH\lessdot^{C_6H_4N(CH_3)_2}_{C_6H_4N(CH_3)_2} + 2C_2H_5OH.$$

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., July 25, 1898.

Formation of Methane-disulphonic Acid during the Reaction of Fuming Sulphuric Acid on Acetylene. — W. Muthmann. — Methane-disulphonic acid, $CH_2(SO_3H)_2$ can be easily obtained by passing a slow current of acetylene through cold fuming sulphuric acid containing 80 per cent of anhydride. It is then thrown into iced water, saturated with $BaCO_3$, filtered, and evaporated. The barium salt is deposited on cooling in the form of flakes containing $2H_2O$. The free acid is in deliquescent needles; the ammonium salt is anhydrous, in the form of very soluble clinorhombic prisms; the potassium salt is analogous to the last.

Methylanilide of Malonic Acid.—D. Vorlaender and P. Herrmann. — Malonylmethylaniline is prepared by heating a mixture of 30 grms. of malonamide and 150 grms. of methylaniline up to 200—240° on an air-bath for six hours. The excess of the base is carried off by a current of steam and the residue is crystallised in ether. The return is 50 grms. Malonylmethylaniline crystallises in tabular prisms fusible at 109°, soluble in alcohol and boiling water, insoluble in HCl. Sodium reacts on a dry benzenic solution of this body, giving rise to a soda derivative soluble in benzene. If this solution is treated with the calculated quantity of iodine, methylaniline of ethanetetracarbonic acid is obtained in the form of white prisms, soluble in alcohol, benzene, and chloroform, and fusible at 231°.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Royal Institution, 5. General Monthly Meeting.
—— Royal Institution. Centenary Day.
—— Society of Chemical Industry, 8. "A New Method for the Analysis of Commercial Phenols," by Dr. S. B. Schryver. A Demonstration of Printing by Electricity without the Aid of Rollers or Ink, by Dr. S. Rideal, F.I.C. "Notes on Cacao Butter," by Dr. J. Lewkowitsch, F.I.C. "The Use of Iron as the Active Element in Primary Batteries used for Electrolysing," by Col. J. Waterhouse, I.S.C.

TUESDAY, 6th.—Royal Institution, 3. Commemoration Lecture by Professor Lord Rayleigh, F.R.S. H.R.H. The Prince of Wales, K.G., Vice-Patron, presiding.
Evening Reception by the Lord Mayor to the Members, Foreign Guests, and Representative Men, at the Mansion House.

WEDNESDAY, 7th.—Royal Institution, 9. Commemoration Lecture by Professor Dewar, F.R.S. His Grace the Duke of Northumberland, K.G., President, presiding.
—— Society of Public Analysts, 8. "On some Comparative Analyses of, and Digestive Experiments with White and Whole-meal Breads," by Otto Rosenheim, Ph.D., and Phillip Schidrowitz, Ph.D. "Note on Coffee Extracts," by C. G. Moor, M.A., F.I.C., and Martin Priest. "On the Determination of the Iodine Value," by J. Lewkowitsch, Ph.D., F.I.C. "On the Influence of Ammonium Salts on the Precipitation of Nickel by Ammonia," by Arthur Marshall.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2063.

THE CRYSTALLINE STRUCTURE OF METALS.*

By J. A. EWING, F.R.S.,
Professor of Mechanism and Applied Mechanics in the University of Cambridge,
and W. ROSENHAIN,
1851 Exhibition Research Scholar, Melbourne University.

In a previous communication read to the Society on March 16, a preliminary account was given of some of the results the authors had arrived at in studying metals by the microscopic methods initiated by Sorby, and pursued by Andrews, Arnold, Behrens, Charpy, Osmond, Roberts-Austen, Stead, and others. The present paper deals with a development and extension of the same work. It relates chiefly, though not exclusively, to the effects of strain, and the relation of plasticity to crystalline structure.

It is well known that the etching of a polished surface of metal reveals, in general, a structure consisting of irregularly shaped grains, with clearly marked boundaries. Each grain is a crystal, the growth of which has been arrested by its meeting with neighbouring grains. This view, as Mr. Stead has pointed out, is strongly supported by the appearance of the etched surface under oblique illumination, when the several grains are seen to reflect light in a way which is consistent only with the idea that on each there is a multitude of facets with a definite orientation, constant over any one grain. but different from grain to grain. The formation of such a structure is well exhibited, on a relatively enormous scale on the inner surface of a cake of solidifying bismuth, from which the still molten metal has been poured away. Another striking example of this structure is seen in steel containing about 4½ per cent of silicon. The fractured ingot of this material exhibits large crystals, and by deeply etching a polished surface Mr. Stead has obtained a beautiful development of the regularly oriented elements of which the crystalline grains are built up (*Journ. Iron and Steel Inst.*, 1898) on a scale so large as to require but little magnification.

The authors have obtained much evidence that this structure is typical of metals generally. Probably under no condition does any metal cease to be crystalline.

The crystalline character of wrought iron bars or plates is seen when the polished surface is etched, not merely by the general appearance of the grains under oblique light, but by the development of geometrical pits on the surface. These pits have a definite orientation over each grain, and the orientation changes from one grain to another. Usually in the purest commercial iron their outline is that of plane sections of a cube, but occasionally they are apparently plane sections of an octahedron. In some instances isolated and comparatively large pits only are seen; in others nearly the whole surface of a grain, when viewed under a magnification of 1000 or 2000 diameters, is found to be covered with small as well as large pits, geometrically similar and similarly oriented. Photographs of these are given in the paper.

For the purpose of producing smooth surfaces in the more fusible metals, without polishing, the metal was poured in a molten state on a plate of smooth glass. The surface produced in this way shows well the boundaries between the grains, and in some cases it also exhibits the crystalline character of the grains in a remarkable way by means of geometrical pits, which are apparently formed on the surface in consequence of the presence of small bubbles of air, or, more probably, of gas given out from the metal itself during solidification. Cadmium shows these particularly well, and they are to be observed also in tin and zinc. These air-pits are seen, under 1000 diameters, to be negative crystals, similar and similarly oriented on each grain, and, in cadmium, to have outlines which suggest that they are sections of hexagonal prisms. Their characteristics are exhibited in the photographs, which also show how the boundaries between the grains are emphasised by the collection there of air or of gas given off by the metal during solidification. The true boundary is merely the trace of a surface on a plane, but it may be broadened out in this way into a wide shallow channel. The effects of strain have been examined in many metals, using surfaces prepared either by polishing or by casting against a smooth plate. When any metal is strained beyond its elastic limit in any way, the surface of each crystalline grain becomes marked by one or more systems of lines running in a generally straight and parallel fashion over it. The direction of the parallel lines changes from grain to grain. Thus these lines serve to mark out one grain from another in a metal which, although polished before straining, has not been etched to develop the boundaries. As straining proceeds, the lines become more and more numerous and emphatic, and two, three, or four systems appear on each grain.

The nature of these lines has been described in the authors' paper of March 16. They are slips along cleavage or gliding planes in the crystals. The effect of each slip is to develop a step on the polished face. The short inclined surface forming this step looks black under vertical illumination, but shines out brightly when oblique light of a suitable incidence is used. These slip bands, as they were named in the previous paper, are thus seen as narrow dark or bright bands, according to the nature of the lighting.

The authors have developed slip-bands in iron, copper, gold, silver, platinum, lead, tin, bismuth, cadmium, aluminium, nickel, as well as steel, brass, gun-metal, and various other alloys. So far as the observations go, they occur in all metals.

The slip-bands are in themselves an evidence of crystalline structure, and, further, they show how such a structure is consistent with plasticity, and how it persists after plastic strain has occurred. The "flow" or non-elastic strain of a metal occurs through numerous finite slips taking place on the cleavage or gliding surfaces in each of the crystalline grains of which the metal is an aggregate. The elementary pieces which slip on one another retain their primitive crystalline character.

Further, if the movement of the pieces with respect to each other in any one grain is a movement of translation only, their orientation should remain uniform in each grain.

That this is actually the case is demonstrated by examining specimens of metal which had been violently deformed without any subsequent annealing or heating. In metal that has been rolled or hammered in the cold state, or deformed by tension or compression or strain of any kind, however severely, the grains are still seen where a surface is polished and etched. Their form is much changed by the strain which the piece has undergone. But the fact that they have retained their crystalline structure is demonstrated when, after polishing, the piece is subjected to a slight additional strain of any kind, for the effect of this additional strain is to develop slips of the same general character as before. Further evidence to the same effect is given by the fact that etching the polished surface of a very severely strained piece develops geometrical pits, which are similar and similarly oriented over the face of each grain, notwithstanding the great distortion which the grain has suffered as a whole. The effects of oblique lighting in metal which is polished and etched after severe straining are referred to as illustrating the same point. The persistence of crystalline structure

* Abstract of the Bakerian Lecture read before the Royal Society, May 18, 1899.

is demonstrated by micro-photographs of the section of a bar of Swedish iron which had been rolled cold from a diameter of ¾ inch to a diameter of ½ inch without subsequent heating. The outline of the grains is much distorted, but the orientation of the crystalline elements remains constant within each individual grain.

The slips in metals which exhibit a cubical crystalline structure on etching are in some instances parallel to the faces of the cubes, and are very frequently inclined to the faces, apparently along the octahedral planes. Stepped lines are frequently seen, and also lines which appear curved probably in consequence of numerous steps which are unresolved even under the highest powers. In exceedingly plastic metals, such as lead, copper, and gold, the lines are particularly straight. A piece of lead cast against glass to produce a smooth surface gives, when slightly strained, a splendid display of slip-bands, and the boundaries of the grains are sharply defined by the meeting of the lines on one grain with those on its neighbours. Another way to get a clear lead surface for the purpose of showing slip-bands is to press a freshly-cut piece of the metal with considerable force against a smooth object. Photographs of slip-bands in iron, gold, silver, lead, copper, and other metals are given in the paper.

When a metal is fractured the grains do not as a rule part company at their boundaries, but split along cleavage surfaces. It is to this that the crystalline appearance, obvious in many fractures, is due.

In several metals the authors find that "twinning" takes place in the crystalline structure as an effect of strain. Samples of copper, which in the original cast state gave no evidence of the existence of twin crystals, were hammered or otherwise wrought, and were then found to be full of twins. The twinning produced in this way survived after the wrought copper had been raised to a red heat and allowed to cool. Similar results were obtained in gold and in silver; the metal in the cast state did not show twins, but they were found after the metal had been wrought and subsequently softened by annealing. An example of twinning was observed in nickel after the application of a somewhat severe strain. Twins were readily developed in cadmium by strain, apparently as a result of the slight strain which was applied for the purpose of developing slip-bands. They were also found in lead, zinc, and tin, either as a primitive feature in the crystallisation or produced by straining. The twinning frequently takes the form of a large number of parallel bands within a single grain, and a twin band due to strain in one grain is sometimes associated with a twin band in neighbouring grains, the bands being continuous except for a change in orientation in passing from grain to grain.

Photographs of twin bands in copper, gold, lead, and other metals are given, showing the twin bands as revealed by a cross-hatching of parallel slip-lines, the sets of lines being parallel to one another in alternate bands of the twin. The twinning under strain which we have observed in various metals is similar to that which is known to occur in calcite. It may be regarded as a result of slip accompanied by a definite and constant amount of rotation on the part of the molecules.

From this point of view there are two modes in which plastic yielding occurs in a crystalline aggregate. One is by simple slips, where the movements of the crystalline elements are purely translatory and their orientation is consequently preserved unchanged. The other is by twinning, where rotation occurs through an angle which is the same for each molecule in the twinned group. Both modes are often found not only in a single specimen of metal but in the same crystalline grain.

At the suggestion of Messrs. Heycock and Neville, the authors' examination of the effects of strain has been extended to certain eutectic alloys. The structure of such alloys has already been described by Osmond, with whose observations these are in agreement. The alloy generally exhibits rather large grains, the structure of which is very different from that of pure metals, for it consists of an intimate intermixture of two constituents, one of which appears as separate or dendritic crystals on a field formed of the other constituent. The two are seen forming an exceedingly minute and complex structure within each of the large grains of which the alloy is made up. Straining has the effect of making this intimate structure more apparent, by causing slips which set up differences of level between pieces of one and the other constituent.

A study of the micro-structure of alloys suggests a possible explanation of the peculiarities they present in regard to variation of electrical conductivity with temperature. The two constituents may behave individually as pure metals in this respect, but if their coefficients of expansion are different the closeness of the joints between them will depend on the temeprature. Thus if the more expansible metal exists as plates, or separate pieces of any form within the other, the effect of heating will be to make the joints between the two conduct more readily, with the result of reducing the increase of resistance to which heating would otherwise give rise, and in extreme cases with the effect even of producing a negative temperature coefficient. The high resistance of alloys generally may be ascribed to the large number of joints across which the current has to pass.

In casting metals against glass and other smooth bodies for the purpose of getting a surface fit for microscopical examination, a surface is occasionally produced which not only shows the true boundaries between the crystalline grains, but also additional markings which simulate boundaries in a very curious manner. These pseudo-boundaries are often polygonal in form, like the real boundaries, and have an intimate geometrical association with them. Under low powers they are in some instances difficult to distinguish from true boundaries; but the distinction is apparent under high powers, and it becomes obvious as soon as slip-bands are developed by the straining of the metal. The pseudo-boundaries are found to consist in small variations of level in the surface of the grains in which they occur. Their form suggests that they are projections upon the surface of real edges below. They occur very conspicuously in cadmium, especially when it is cast on a cold surface, and less conspicuously in zinc. It is probable that in the strain set up by unequal cooling after the metal has solidified, the lower edges of the crystalline grains project a sort of image of themselves on the surface by slips, or possibly by narrow bands of twinning. The effect resembles that of a Japanese "magic" mirror, in which slight inequalities of the surface, corresponding to a pattern behind, cause light reflected from the mirror to produce an image in which a ghost of the pattern may be traced.

The authors regard their experiments as establishing the conclusion briefly stated in their previous paper, to the effect that the plasticity of metals is due to the sliding over one another of the crystalline elements composing each grain, without change in their orientation within each grain, except in so far as such change may occur through twinning.

ON A TUNGSTO-POTASSIC TUNGSTATE.

By L. A. HALLOPEAU.

I HAVE already (*Bull. Soc. Chim.*, Series 3, vol. xix., 745) established the fact that hydrogen reduces paratungstate of potassium, giving a compound with the formula $K_2O,WO_3+WO_2.WO_3$.

We obtain a tungsten bronze, of a different composition, by the reduction of the acid tungstate of potassium by tin. The experiment is performed very easily by heating paratungstate of potassium for an hour with a small quantity of tin. The operation should be carried out in a porcelain crucible in a muffle furnace, heated to

a temperature high enough to melt the tungstate. The melted mass is treated successively with boiling water, concentrated hydrochloric acid, and a boiling solution of carbonate of potassium at 50 per cent. After a final washing with warm water, a pulverulent substance remains having a very deep blue colour. Under the microscope we see that this matter is composed of prismatic crystals; they answer to the formula $K_2O,WO_3 + WO_2,3WO_3$. By its constitution this body resembles the tungsto-lithic tungstate $Li_2O.WO_3 + WO_2.3WO_3$, which I have already described in a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xix., p. 953), and the tungsto-sodic tungstate, $Na_2O.WO_3 + WO_2\ 3WO_3$, which occurs in blue prismatic crystals like the preceding ones, and which was obtained by Philipp by fusing the acid tungstate of sodium with tin for a short time. In preparing this substance care must be taken not to prolong the action of the tin on the melted acid tungstate.

Philipp has shown that if we keep the tin in the presence of fused acid tungstate of soda for a sufficiently long time, we no longer obtain the same compound. It is Wohler's salt which is formed, $Na_2O.WO_3 + WO_2.WO_3$. This fact has already been observed by Wright.

On carefully examining the tungsto-potassic tungstate prepared by means of tin, we also observe here and there a few violet-red prisms, similar to the crystals obtained by reduction by hydrogen, but they are in excessively small quantity. I have in vain tried to obtain a greater proportion of them by prolonging the action of the tin on melted paratungstate of potassium. If the duration of the experiment is increased a total reduction of the potassium salt takes place: after six hours' heating, I found a greyish powder formed of a mixture of metallic tungsten and of crystallised binoxide of tin.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 6.

THE VOLUMETRIC ESTIMATION OF CARBON.

By HENRI IMBERT and P. COMPAN.

We undertook the following experiments with a view to the estimation of the pure carbon deposited in very thin layers on sheets of glass.

The process depends on the following facts:—

A sulphuric solution of chromic acid oxidises carbon, giving carbonic acid and chromic sulphate. By disregarding the sulphuric acid we can represent the reaction by the formula—

$$(1).\quad 3C + 4Cr_2O_3 = 2Cr_2O_3 + 3CO_2,$$

from which it follows that 36 of carbon corresponds to 400 of chromic acid reduced. Again, a sulphuric solution of chromic acid acts on iodide of potassium in excess, setting iodine at liberty according to the equation—

$$(2).\quad 2CrO_3 + 6KI + 3H_2O = Cr_2O_3 + 6KOH + 3I_2.$$

100 of CrO_3 sets free $3 \times 127 = 381$ of iodine, which can be titrated by means of hyposulphite of soda.

Extremely small quantinies of carbon can be estimated by this process.

We operated in the following manner:—

A known weight of carbon, placed in a beaker, is treated with a known excess of a titrated solution of chromic acid, and a little sulphuric acid at 4 per cent; the solution is first evaporated on a sand-bath, then—when it is brought to a small volume—on a water-bath.

The colour does not appear to be modified until the liquid takes a syrupy consistence, but at this moment it shows a yellow to a greenish-yellow tint (a decided greenish-blue tint indicates that the quantity of chromic acid used is insufficient); under these conditions the carbon is entirely consumed. The residue, diluted with water, is then placed in a glass bromine bulb; we add iodide of potassium in excess, and, if the iodine is not set at liberty, a further quantity of sulphuric acid at 4 per cent is added. The liquid is exhausted four or five times with sulphide of carbon, which is collected in a glass-stoppered flask: when this exhaustion is complete, the sulphide of carbon remains colourless, and the supernatant liquid has a greenish-blue tint.

The sulpho-carbonic solution of iodine is agitated with bicarbonate of soda at 5 per cent, to neutralise the free sulphuric acid, and then titrated by means of hyposulphite of soda with the usual precautions.

From the volume of hyposulphite employed we deduce the chromic acid remaining, and, by difference, that used. According to equation (2) we calculate the weight of carbon which has been consumed.

We have operated on successive weights of carbon of 0·018, 0·040, and 0·025 grm., and have found 0·0171, 0·0388, and 0·02422 grm.

This carbon was prepared by the deposition of lamp-black on a sheet of glass, which was subsequently washed with alcohol (Crova and Compan, *Comptes Rendus*, cxxvi., 707) to remove pyrogenous products; the concordance of the results shows that the carbon was practically pure.

This method is of very great sensitiveness; in operating on a solution of 3·81 grms. of hyposulphite of soda per litre, corresponding to 1·945 grms. of iodine, we can very easily recognise the complete decolouration of the sulphide of carbon to one drop: now 0·0111 grm. of chromic acid corresponds to 0·0423 grm. of iodine and to 0·001 grm. of carbon.

Between two successive operations carried out on the same volume of CrO_3, before and after reduction by carbon, 0·001 grm. of the former corresponded to a loss of 0·0423 grm. of iodine set at liberty, and consequently to a difference of 21·7 c.c. of hyposulphite used.

We then operated on a microscopic cover-glass, covered with a thin film of alcohol-washed lamp-black. The titrated solutions corresponded to the hyposulphite solution at 3·8 grms. per litre, and we were thus able to estimate 0·0013 grm. of carbon deposited. The sensitiveness of the method, in our opinion, enables us to accurately estimate 1 m.grm.

In devising this method we had to consider the estimation of chromic acid by the liberation of iodine, an iodide, and the titration of the iodine.

The results obtained corresponded very accurately with those obtained by ponderable means, by precipitation in the state of chromate of lead.

The facility with which the iodine is set free in the cold, by a sulphuric solution of chromic acid, has led us to effect the separation of bromine from iodine by this reagent. We operated successively on—

10 c.c. of a solution of iodine						
10	,,	,,	,,	+ 10 c.c. of a solution of bromine		
10	,,	,,	,,	+ 20	,,	,,
10	,,	,,	,,	+ 30	,,	,,

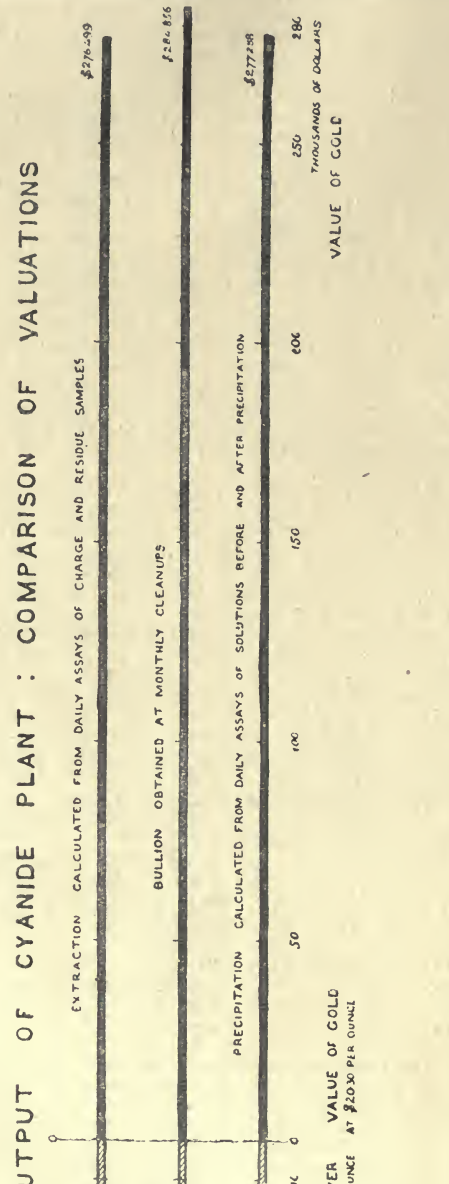
The volume of the titrated solution of hyposulphite of soda necessary for the decolouration of the sulphide of carbon was 9·80 c.c. for each of these operations, no matter what excess of sulphuric and chromic acids was used. The bromine is, therefore, not set free under the conditions of the experiment; we simply experienced a little more difficulty in the exhaustion with the sulphide of carbon. It is not till after twenty-four hours after the separation of the iodine that the sulphide of carbon left in contact with the solution becomes coloured faintly yellow.

We therefore think that M. Carnot's process, recently described in the *Bulletin* (Series 3, xix., 251), might be modified by substituting, in the separation of the bromine and iodine, a cold sulphuric solution of chromic acid for the nitrous sulphuric acid.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 6.

NOTES ON THE ALLEGED SHORTAGE IN CYANIDE BULLION.*

By C. W. MERRILL, Assoc. Inst. M.M.

THE impression that the bullion returns from cyanide plants are, in spite of the observance of all possible precautions, uniformly less than the correct tonnage multiplied by the difference between the values per ton indicated by assays of the "charges" and "residues," seem to have become so general that it was thought that the accompanying plan, with a brief explanation as to how the figures were computed, would be of interest.



The figures are the results from the operations from July, 1897, to November, 1898, of the tailings plant of the Montana Mining Co., Ltd., the capacity of which is 12,000 tons per month.

About 125 truck-loads, of 3 tons each, are treated daily; from six to ten of these loads are weighed, and large samples taken from each; the accumulation of these car-moisture samples gives the average daily moisture sample. From the number of loads dumped, the average weight per load, and the moisture per cent, is calculated the number of dry tons treated daily.

The sand passes from the cars to the bins, and thence by belt conveyors into a rotary distributor over the centre of each vat. The stream of sand is sampled three times an hour for nine hours, the time taken to fill a 400-ton vat. This large sample is quartered down, and four assay tons of the dried sample are taken for duplicate melts and weighings of gold and silver. If the variation in the weights of gold obtained from these two melts does not exceed 1/50 m.grm., the average is taken as the value per ton of the tailings charged that day; otherwise the assays must be repeated.

After treatment, 16 cores are taken from the residue in the vat; this sample, weighing several hundred pounds, is in turn cored, giving about 20 lbs., which is dried, mixed, and quartered, for the final assay sample. If the final weighings differ by more than 1/50 m.grm., the assays must be repeated.

The monthly output calculated on the basis of the preceding determinations are shown in the upper line of the accompanying figure, the gold being to the right of the datum line, and the silver to the left.

The total amount of unprecipitated solution is measured, sampled, and assayed, as is also the precipitated solution. The solutions are evaporated down to a small bulk, a much larger quantity of the latter than of the former being taken; a mixture of litharge, silica, and charcoal added, and the whole heated till dry; after cooling, carbonate of soda is added, and the whole placed in a crucible, melted, and assayed. These solution assays are of great practical utility, not only as guides to the efficiency of the precipitation, but also as giving warning of the presence of reducing material in any charge several days before the residue from such a charge is available for assay; they are made primarily for these reasons.

The estimation of the values recovered monthly on the basis of these solution assays is shown on the lower line of the figure.

The monthly bullion assays are made with the usual precautions, including determination of the cupel absorption, check for volatilisation of silver, &c., and are shown in the centre line of the figure. A shortage of bullion is usual in the first clean-up, the deficiency being made up in the succeeding months.

The total value of gold and silver required by the daily assays is 328,096·21 dollars, and that actually recovered is 337,428·62 dollars, or an excess of 2·84 per cent over the estimate—a highly satisfactory concordance.

* Abridged from a Paper read before the Institution of Mining and Metallurgy, April 19, 1899.

Ratio of the Atomic Weights of Hydrogen and Oxygen.—A. Leduc.—The synthesis of water by weight has led the author to the conclusion that 15·88 is the exact relation between the atomic weights of oxygen and hydrogen. Another method, founded on the determination of the densities of the two gases (both separate and mixed together in the proportion to form water), has given a result (15·868) distinctly lower than that given above. This latter result is probably due to the increase of pressure produced when 2 vols. of H are mixed with 1 vol. of O.—*Comptes Rendus*, cxxviii., No. 19.

THE DETERMINATION OF POTASH AS PERCHLORATE.*

By F. S. SHIVER.

The increasing use of potash salts for fertilising purposes has made the determination of potash a question of prime importance to the agricultural chemist.

The desire to devise a method at the same time rapid and accurate has been manifested in many ways in the past few years, especially in Germany, the seat of the great potash deposits.

The German chemists believe they have solved the problem in the so-called Stassfurt method, which, as all know, permits of the separation of the potash by platinum chloride after previous precipitation of sulphuric acid by barium chloride in slight excess, and in a strongly acid solution. This method, with practice, is quite accurate and rapid, with a slight tendency, however, to high results in my hands. It possesses little advantage over the Lindo-Gladding method, in so far as rapidity and accuracy are concerned.

The following determinations were made by the Stassfurt method—potassium sulphate, C.P., and potassium chloride, C.P., were mixed with such impurities as to imitate the composition of commercial sulphate of potash, sulphate of potash and magnesia, kainit, and muriate.

Table I.

	K_2SO_4 used. Grm.	K_2SO_4 found. Grm.	Error on K_2SO_4. Grm.	Error on K_2O. Grm.
Sulphate of potash	0·3284	0·3291	+0·0007	+0·0004
		0·3289	+0·0005	+0·0003
Sulphate of potash and magnesia ..	0·1856	0·1863	+0·0007	+0·0004
		0·1870	+0·0014	+0·0008
Kainit	0·1000	0·1003	+0·0003	+0·0002
		0·1009	+0·0009	+0·0005
	KCl used. Grm.	KCl found. Grm.	Error on KCl. Grm.	Error on K_2O. Grm.
Muriate	0·2506	0·2498	−0·0008	−0·0005
	0·2522	0·2514	−0·0008	−0·0005

The factor used for converting potassium platinichloride into potassium sulphate was 0·35694, which is practically the same as that recommended in the Stassfurt method, viz., 0·357. The factor used for converting potassium platinichloride into potassium chloride was 0·30557, which is practically the same as that recommended in the Stassfurt method, viz., 0·3056. It will be seen from the above results that the method is quite accurate, with a tendency, however, to slightly high results.

In view of the increasing importance of the potash determination, it is highly desirable that we should possess a check method, rapid and accurate, based on some other principle of separation than that with platinum chloride.

All of our present methods for the determination of potash involve the use of platinum chloride as a means of final separation, and hence they are all subject to the same general sources of error, such as solubility of the platinichloride in the 80 per cent wash alcohol used, &c.

Of all the salts which potassium forms with acids, none are as well adapted for furnishing the basis of another process as the perchlorate, which is nearly insoluble in strong alcohol.

As all the compounds which perchloric acid forms with the bases other than potash and ammonia are soluble in alcohol, we may readily deduce the basis of another process. The determination of potash as perchlorate is an old process due to Sérullas, who first noticed the insolubility of the salt in alcohol, and to Schlœsing, who made it the basis of a new process. Schlœsing's process, improved later by Kraut, has, however, not come generally into use, since the same produces inaccurate results.

W. Wense (*Zeit. Angew. Chem.*, 1891, 691; and 1892, 233) has made the process useful, since he diminishes the solvent action of the alcohol on the perchlorate through the addition of slight quantities of perchloric acid. He describes the following course of procedure:—

The solution to be investigated is evaporated, after once freeing it of sulphuric acid and non-volatile acids with perchloric acid in a porcelain dish. In order to wash the perchlorate easily, it is desirable to produce the same in a granular condition. This is attained by warming the solution containing the potash on a water-bath before adding the perchloric acid, which must be run in drop by drop. In all cases there are used about one and a half to one and three quarters times the amount of perchloric acid necessary for the decomposition of the salt present.

After the addition of the perchloric acid, the solution is evaporated until all odour of hydrochloric acid or other volatile acids has disappeared. For washing the precipitate 96 per cent alcohol is used, to which two-tenths per cent of its weight in perchloric acid is added.

The residue from the evaporation is treated with 10 c.c. of the alcoholic wash solution, which may take up only 1/20,000th of a part of potassium perchlorate, and the salt mass is then broken up with a stirrer.

Decantation is performed through a weighed filter, which has been previously dried at 120—130° C., when the breaking-up of the salt mass is repeated, and the residue again treated with the alcohol wash solution. The precipitate is then brought on the filter, and freed of the adhering perchloric acid solution by washing with a few c.c. of pure alcohol. The filter is then pressed between folds of filter-paper, dried for twenty-five minutes at 120—130° C., and weighed.

One part of potassium perchlorate corresponds to 0·5382 part of potassium chloride, and 0·6289 part of potassium sulphate.

According to the author, the whole washing with a good pump occupies only a short time, and requires 50 to 70 grms. of alcohol. If the substance to be investigated contains sulphuric acid, the same is to be removed in the usual way by barium chloride previous to the determination of the potash. The author, who used the method in the investigation of potassium chloride, C.P., commercial muriate, kainit, and carnallite, obtained—according to the analyses reported—very favourable results.

R. Caspari (*Zeit. Angew. Chem.*, 1893, 68) recommends collecting the potassium perchlorate in tubes containing asbestos filters, and subsequent drying for twenty minutes at 130—150° C. The tubes are allowed to cool in a desiccator or in the air and then weighed.

According to Caspari, the method is applicable for fertilisers, ashes, and the like, in the presence of phosphoric acid, alkaline earths, iron, alumina, and manganese, if the following method of procedure is adopted:—

After the removal of sulphuric acid, the hydrochloric acid solution is evaporated for the purpose of getting rid of the free acid, the residue stirred with 20 c.c. of hot water, after which perchloric acid is added in quantity not less than one and a half times that necessary for the decomposition of all salts present.

The solution is now evaporated with frequent stirring to a syrupy consistency, some hot water is again added, and the solution evaporated still again with occasional stirring until the disappearance of all odour of hydrochloric acid, and till the appearance of white fumes of perchloric acid. An evaporation of large quantities of perchloric acid is to be avoided; if this takes place, more perchloric acid is to be added.

The cooled, more or less syrupy, contents of the dish are well stirred up with about 20 c.c. of wash alcohol (96 per cent alcohol containing two-tenths per cent perchloric acid), taking care, however, not to reduce the potassium perchlorate to a fine powder. After the alcoholic solution has become clear, it is decanted through the asbestos

* *Journal of the American Chemical Society*, xxi., No. 1.

filters, the washing repeated with the same quantity of wash alcohol, allowed to settle, and decanted again.

The residue remaining in the dish is freed of alcohol by gently warming, evaporating again with about three-tenths grm. of perchloric acid and a little water, and washing the cooled mass with several c.c. of alcohol, with which it is also brought into the filters and the perchlorate in the tubes finally covered with a little pure alcohol. The potassium perchlorate obtained in this way contains, according to Caspari, no phosphoric acid, or only slight quantities of the same; on an average only 0·00057 grm. phosphoric acid.

In the separation of sulphuric acid, Caspari seeks to avoid, as much as possible, a loss of potash, since he precipitates in a strong hydrochloric acid solution at the boiling temperature with a concentrated solution of barium chloride made acid with hydrochloric acid. Experiments of the author prove also the applicability of the method in the presence of other acids not volatile on the water-bath, as chromic acid, and also boric, tartaric, and oxalic acids. If ammonium salts are present, they are to be removed either with soda-lye or milk of lime, by gentle heating or through careful ignition.

A. Kreider (*Am. Journ. Sci.*, xlix., 443) has followed the method as described by Caspari, and has obtained very satisfactory results. Kreider found the Gooch crucible preferable in the filtering of the perchlorate, and recommends the same instead of the tubes proposed by Caspari. In the presence of phosphoric acid, the previous separation of which is not necessary, it appeared advisable, according to Kreider's experiments, to allow the perchlorate precipitate to stand with an excess of perchloric acid before treating with alcohol.

Six determinations made of potassium unmixed with other bases or non-volatile acids gave the following results:—

In two cases the theoretical amount of potash (K_2O) was recovered as perchlorate; in three cases there was a loss of 0·0002 grm.; and in one case a loss of 0·0003 grm.; one-tenth grm. of potassium chloride was operated on in all cases. In order to repeat Kreider's work, and to ascertain the accuracy of the process, the following work was undertaken. A solution of chemically pure potassium chloride was prepared by dissolving 1·0005 grms. in 200 c.c. water. 1 c.c. of the solution was found to contain 0·005 grm. potassium chloride, aliquot portions being measured from a burette, evaporated, dried, and weighed.

In all the work here reported, the method as proposed by Caspari, with the use of the Gooch crucible, as suggested by Kreider, was employed.

However, in the first three experiments reported, the perchlorate was collected on paper filters as suggested by Wense, washed in the usual way, dried, and the perchlorate dissolved in hot water, and the solutions evaporated to dryness in platinum dishes and weighed.

In all cases the weighed perchlorate was a little discoloured, due to the fact that the paper filters had been acted on to a slight extent by the perchloric acid, causing them to char a little around the edges during the process of drying. In the subsequent leaching with hot water, some of this carbonaceous material dissolved, and went in solution with the perchlorate.

The results obtained by weighing in dishes as above described were as follows:—

TABLE II.

	KCl solution used. C.c.	Equivalent to KCl. Grm.	KCl found. Grm.	Error on KCl. Grm.	Error on K_2O. Grm.
I. ..	6·2	0·0310	0·0310	+0·0000	+0·0000
II. ..	8·1	0·0405	0·0411	+0·0006	+0·0004
III. ..	5·0	0·0250	0·0253	+0·0003	+0·0002
Average ..		0·0322	0·0325	+0·0003	+0·0002

It will thus be seen that the average error in these determinations is 0·0003 grm. KCl; it is possible that this slight plus error is due to the slight discolouration already noticed, and the weighing in dishes is not to be recommended, though the results obtained are sufficiently accurate for all practical purposes. In the other experiments which follow, the potassium chloride was weighed out directly for analysis, and the perchlorate was collected always in a Gooch crucible.

TABLE III.

	KCl used. Grm.	KCl found. Grm.	Error on KCl. Grm.	Error on K_2O. Grm.
I.	0·0848	0·0859	0·0011	+0·0007
II.	0·0217	0·0217	0·0000	0·0000
III.	0·0419	0·0413	−0·0006	−0·0004
IV.	0·1007	0·1009	+0·0002	+0·0001
V.	0·1003	0·1015	+0·0012	+0·0008
VI.	0·1016	0·1015	−0·0001	−0·0000
VII.	0·0217	0·0210	−0·0007	−0·0004
Average..	0·0675	0·0677	+0·0002	+0·0001

In the above determinations No. 1 was among the first made, and it is possible that the slightly high results obtained were due to lack of familiarity with the method. Excluding No. I., the average would be as follows:—

KCl used. Grm.	KCl found. Grm.	Error on KCl. Grm.	Error on K_2O. Grm.
0·0647	0·0647	0·0000	0·0000

It would thus appear that the determination of potash as perchlorate in mixtures free from other bases and non-volatile acids, is quite accurate, equally as much as the determination by platinum salt.

After nitrogen and phosphoric acid, potash is the compound one has mostly to determine in fertilisers, plants, and soils. The potash is usually combined with sulphuric, nitric, or carbonic acid, and more rarely with phosphoric acid.

These salts are almost always associated with alkaline salts and the alkaline earths. It is now therefore a question of the applicability of the perchloric acid method to the determination of potash when associated with these other bases and non-volatile acids, such as sulphuric and phosphoric acid. In regard to the bases, it has been contended by some that magnesia is a disturbing element in the determination of potash by perchloric acid.

Schlœsing has shown, however, that in the following mixture, after the removal of sulphuric acid by barium chloride and conversion of bases into perchlorates, the magnesia did not have any disturbing effect.

Potassium chloride	0·0835 grm.
Magnesium sulphate	0·5740 ,,
Sodium chloride	0·1298 ,,
Calcium chloride	0·2330 ,,

In this mixture there was recovered, by proceeding as above stated, 0·0814 grm. potassium chloride. Kreider has also shown that magnesia has no disturbing effect. He treated 0·1500 grm. magnesium carbonate with perchloric acid, evaporated till fumes of perchloric acid appeared, and cooled, when magnesium perchlorate crystallised; on treating this with alcohol, a perfectly clear solution was obtained. It was also thought that it was necessary to remove all non-volatile acids previous to the separation of the potash as perchlorate. Caspari and Kreider have, however, shown that it is only necessary to remove sulphuric acid. In order to secure a nearly complete separation of phosphoric acid from the potassium, Kreider has shown that a considerable excess of perchloric acid should be left upon the potassium perchlorate before it is treated with the alcohol.

Kreider's results on a mixture containing—

Potassium chloride	.. ..	0·1 grm.
Magnesium sulphate	.. ..	0·13 ,,
Aluminum sulphate	.. ..	0·05 ,,
Sodium phosphate	.. ..	0·4 ,,
Calcium carbonate	.. ..	0·13 ,,
Ferric chloride	.. ..	0·05 ,,
Manganese dioxide	.. ..	0·05 ,,

were quite promising, as will be seen from the results reported in the *American Journal of Science*, xlix., 448.

The method as modified by Caspari and Kreider is quite promising, and I hope in the near future to do some further work on the determination of potassium associated with other bases and non-volatile acids.

(To be continued).

PRESIDENTIAL ADDRESS TO THE IRON AND STEEL INSTITUTE.

By Professor Sir W. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S.

(Concluded from p. 259).

1885-87. In no other branch of modern scientific literature than that of metallurgy does one individual stand far above his contemporaries and absolutely dominate his subject as does Dr. John Percy. It may be fairly claimed that he did this, for he truly represents the progress of metallurgical literature during the nineteenth centurv. He was also the century's greatest teacher; he found metallurgy practised in this country as an empirical art, His splendid works contain a record of its progress; his lectures at the Royal School of Mines secured it a scientific basis, and he trained a body of workers in whose hands the immediate future of metallurgy still, to a great extent, rests. To few men does the nation owe more than to our President of 1885-87. The educational work Dr. Percy began is being actively developed. As regards its progress in the future—which is of vital importance—there seem to me to be no requirements that may not be abundantly met by the extension of existing institutions. The establishment of a Board of Mining and Metallurgy in connection with the new Teaching University for London, would, I am satisfied, greatly sitimulate instruction in these subjects.

1887-89. Daniel Adamson will be known rather as a mechanical engineer, and the originator of the Manchester Ship Canal, than as a metallurgist. His Presidency of this Institute is, however, remarkable for his strenuous advocacy of the use, not only of steel as distinguished from iron, but that for definite purposes steel of a definite degree of carburisation and suitable composition should be employed. He also eloquently urged that the steel at all stages of its manufacture in its varied applications should receive suitable thermal treatment. He strongly advocated the use of steel for the manufacture of boilers, and he pointed out that by the use of steel rails and weldless solid rolled steel tyres, the saving to railway shareholders amounted to about £3,120,000 sterling per annum, while the safety and security of the travelling public had been correspondingly increased. No better indication of progress in the decade ending 1889 could well be given than this.

1889-91. The vast advance during the century in the applications of iron and steel in the manufacture of machinery, and more especially to locomotives, is fittingly represented by Sir James Kitson. We, moreover, owe him a deep debt of gratitude for the admirable way in which he represented the Institute by presiding at the Autumn Meeting of the Institute in Paris in 1899, as well as during the arduous but most remarkable visit to the United States in 1890. Sir James, by his unflagging vigour and unfailing tact, did much to cement the friendship of workers in iron and steel, both among our neighbours in France and our kinsmen in America. I will only add that he has persistently advocated the use, and has well maintained the reputation, of that admirable material, "best Yorkshire iron."

1891-93. One of the most noteworthy events in the metallurgical progress of this country was the acceptance by Sir Frederick Abel of the post of Chemist of the War Department. The teaching of such illustrious men as Berzelius, Heinrich Rose, and Liebig was just in process of thorough application in this country when Abel left our matchless teacher Hofmann to take his place among the earliest trained analytical chemists whose aid was sought by the ironmaster. He thus became, as it were, the "Patron" of works chemists. They are men on whose patient, monotonous, and often inadequately recompensed, labours the quality of British iron and steel has in no small measure depended, and I am glad to have this opportunity for offering my brethren, the chemists in works, a respectful tribute of admiration. The magnitude of their work may be gathered from the fact stated in the *Journal* of our Institute, that in one basic steel works over 110,000 determinations are made in a single year by three chemists and six assistants. Of Sir Frederick's numerous investigations, the one which appeals to us most closely is that which definitely settled, as Fe_3C, the composition of carbide of iron.

Lord Herbert of Lea, who was several times Secretary for War and was in office soon after Sir Frederick was appointed to Woolwich, appears to have been advised that "steel was wholly inapplicable for the manufacture of ordnance." When we consider what the nature of our present war material is, and reflect how large a part Abel played in its introduction and adoption, it will be evident that any further comments of mine as to the value of his labours would be unnecessary. He is himself a most active exponent of the truth "that the intimate blending of science with practice lies at the root of all industrial progress and success."

1893-95. I am quoting from an American source the testimony that "an historical sketch of the perfecting of modern processes of steel manufacture would afford the best glimpse that could be given of the career of Edward Windsor Richards." He was among the first to appreciate the need for reversing mill-engines, and an early one erected by him is still at work at Ebbw Vale. He designed the works of Messrs. Bolckow, Vaughan, and Co., at Middlesbrough, the largest in the kingdom, and as general manager of the famous Low Moor Works has fully maintained its reputation for the production of one of the most famous varieties of iron in the world. His connection with what is known as the basic process will be alluded to later on. In view of the fact that appliances will handle and forging presses deal with weights of steel up to 100 tons, he long ago anticipated the possibility of making 10 tons of steel into one ingot.

1895-97. The progress of an industry during the century can only be adequately indicated by the evidence afforded by statistics. In this respect no more comprehensive statements could have been desired than those embodied in the Presidential Address of Sir David Dale. Sir David has, however, secured a firmer claim to the gratitude of the nation than that which is derived from his powers as a statistician. He has from time to time been the trusted arbitrator between masters and men, and as Chairman of one Section of the Labour Commission (1891-94) rendered admirable services in the interests both of capital and labour. He was also the representative of this country at the Berlin Labour Congress of 1890. His work has, moreover, enabled us to trace, in the last twenty years of the century, the progress of the spirit of equity among all sorts and conditions of men, who have gladly borne testimony alike to his firmness and his justice. His efforts have been unwearyingly directed to removing difficulties which have from time to time arisen between employers and the employed. I need

hardly allude to his long services as Treasurer of this Institute, nor do you need to be reminded that we owe the ability to carry on our work efficiently to his careful husbanding of our resources.

1897-99. To the foresight of Edward Pritchard Martin we owe the adoption in practice of one of the great processes which will render the nineteenth century memorable. I refer to what is collectively called the "Basic process." It would be impossible to trace its history now. I prefer in any reference, which must of necessity be so brief, to appeal to the appreciative words in the paper which Sidney Thomas and Percy Gilchrist communicated to our Institute in 1879. They then stated that, "on laying some of the first results obtained from this six-pound converter before Mr. Martin of Blenavon, he at once recognised their importance, and from that time we have been deeply indebted to him for his unfailing and consistent support and much valuable advice and assistance." It need only be added that the metallurgical world is also under a lasting debt of gratitude to Mr. Martin. Later on other aid was as gratefully recognised. Mr. Thomas said, on the occasion of his receiving the Bessemer Medal (1883), "the present position of dephosphorisation has only been rendered possible by the frank, generous, and unreserved co-operation of Mr. Windsor Richards, and of our earlier and consistent supporter Mr. Martin." All those I have named have received the Bessemer Medal. We lost Sidney Thomas far too soon. Mr. Snelus, to whose work I have already referred, and Mr. Gilchrist received the highest honour the scientific world has to bestow—the Fellowship of the Royal Society.

The introduction of labour-saving machinery in the great Dowlais Works, which Mr. Martin directs, marks an era in British metallurgy.

This conclues the list of those who have hitherto presided over this Institute, and it will have been evident that from time to time other interests than those connected with iron and steel have been represented by your Presidents. We were reminded of this fact when the Institute first met, now twenty-four years ago, at Manchester, where we are promised a delightful meeting again next autumn. The Bishop of that great city then welcomed us by a quotation from Virgil, which connects the age of iron with the age of gold. The passage runs thus:—

"*quo ferrea primum*
Desinet ac toto surget gens aureo mundo."

A President of this Institute who has had the privilege to serve in the Mint in a sense connects the iron and the golden age. I find that during the course of a long official career I have been responsible for the standard fineness of over one hundred and twenty-one millions of gold coin. This sum is so vast, and the anxiety connected with it has been at times so great, that I am not careful to conceal the pride revealed by this reference to it, as it is an exponent of the financial greatness of the nation which created the age of steel. But I value as highly the means of conducting research and the hope of being useful, which was also given me by the Government when I was appointed Professor of Metallurgy at the Royal School of Mines. I have in the discharge of my duties persistently striven to show that what is called applied science is nothing but the application of pure science to particular classes of problems.

I regret that space will not permit me to consider the progress of the century as measured by the work of our Bessemer Medallists. I hope, however, as regards the labours of the foreign recipients of the honour, to deal with them next spring. The metallurgy of America is so closely interwoven with our own, that I must permit myself a brief reference to four men who stand out from the industrial ranks of our kinsmen. These are Alexander Lyman Holley, the Hon. Abram S. Hewitt, John Fritz, and Professor Henry Marion Howe. All of them are Bessemer Medallists.

I only once had the good fortune to see the winsome pioneer of the Bessemer process in America, "our dear Holley," if I may borrow and adopt the phrase used to me by one of the American members at Stockholm last autumn, with reference to one the charm of whose character was neither impaired by difficulty or by success. All Holley did for the Bessemer process is fully recorded in our *Journal*, and it is only necessary to state that, from the time the first charge was blown at the Troy Works in 1865, there have been produced in America over sixty-one million tons of Bessemer steel.

It was in the works of the Hon. Abram S. Hewitt that the first Bessemer converter was installed, and Mr. Hewitt was also the first to build an open-hearth furnace in the United States.

Mr. John Fritz was one of the small band of leaders who so successfully developed the Bessemer process in the United States, and excited the admiration of the metallurgical world by large outputs from comparatively small installations. He also aided in designing one of the most important arsenals in the world, where the highest quality of open-hearth steel was produced.

Of the labours of my friend, Professor Henry Marion Howe, it would be difficult to speak adequately. As an experimental investigator he has greatly added to our knowledge of the properties of iron and steel. In the field of literature he has left on record a monumental work which enables him to rank with Dr. Percy as the metallurgical historian of the Anglo-Saxon race.

It may help us to estimate the value of the labours of the four men whose names I have given if we remember that at the present time the United States export about a million tons of iron and steel a year, while twenty years ago they were not exporting any. We may fairly consider, therefore, their influence on the rapid development of the United States navy. It would seem that we, in this country, in the belief in our insular security, had somewhat neglected the art of naval warfare, until Admiral Mahan reminded us of what we had done in the past, and of our possible course in the future, in a series of writings which have done much to convince the two nations, England and America, "that they are in many ways one."

It is time to offer a collective statement of the achievements which have either been actually effected or are in immediate prospect.

There are blast-furnaces which will produce 690 tons of pig-iron in twenty-four hours, with a consumption of little over 15·4 cwts. of coke per ton of iron. The gases from blast-furnaces are used not only as sources of heat, but directly in gas-engines.

There are Bessemer converters which can hold 50 tons of metal, and open-hearth furnaces which will also take 50 tons, while 100-ton furnaces are projected. The open-hearth furnaces are fed with 1 ton of material in a minute, by the aid of a large spoon worked by an electro-motor. There are gigantic "mixers," capable of holding 200 tons of pig-iron, in which, moreover, a certain amount of preliminary purification is effected.

Steel plates are rolled of over 300 feet in area and 2 inches thick. There are girders which justify the belief of Sir Benjamin Baker, that a bridge connecting England and France could be built over the Channel in half-mile spans. There are ship-plates which buckle up during a collision, but remain water-tight.

There are steel armour piercing shot which will penetrate a thickness of steel equivalent to over 37 inches of wrought iron. The points of the shot remain intact, although the striking velocities are nearly 2800 feet a second. There are wires which will sustain a load of 170 tons per square inch without fracture. Hadfield, whose labours will, I trust, be continued far into the twentieth century, has given us manganese-steel that will not soften by annealing; while Guillaume has studied the properties of certain nickel-steels that will not expand by heat, and others that contract when heated and expand when cooled,

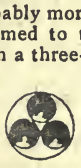
Nickel, chromium, titanium, and tungsten are freely used alloyed with iron, and the use of vanadium, uranium, molybdenum, and even glucinium, is suggested. There are steel rails which will remain in use seventeen years, and only lose 5 lbs. per yard, though fifty and a half million tons of traffic have passed over them.

Huge ingots are placed in soaking pits and forged direct by 120-ton hammers, or pressed into shape by 14,000-ton presses. With such machinery the name of our late Member of Council, Benjamin Walker, will always be connected.

There are steel castings for parts of ships that weigh over 35 tons. We electrically rivet and electrically anneal hardened ship-plates that could not otherwise be drilled. Photomicrography, originated by Sorby in 1864, now enables us to study the pathology of steel, and to suggest remedial measures for its treatment. Stead's works in this field is already recognised as classical. Ewing and Rosenhain have, in a beautiful research, recognised quite recently by its aid that the plasticity of a metal is due to "slip" along the cleavage planes of crystals. Osmond also by its aid shows that the entire structure of certain alloys may be changed by heating to so low a temperature as 225° C.

Passing to questions bearing upon molecular activity, we are still confronted with the marvel that a few tenths per cent of carbon is the main factor in determining the properties of steel. We are, therefore, still repeating the question, "How does the carbon act?" which was raised by Bergman at the end of the eighteenth century. Nevertheless, from the molecular point of view, much may be said in answer to the question. The mystery is in fact lessened now, as it is known that the mode of existence of carbon in iron follows the laws of ordinary saline solutions. Our knowledge is, however, of very recent origin, and we owe mainly to the Alloys Research Committee of the Institution of Mechanical Engineers the development of Matthiessen's view that there is absolute parallelism of the solution of salt in water and carbon in iron.

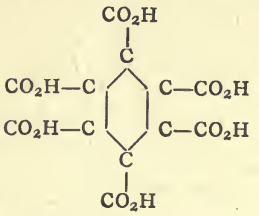
An ice-floe in a Polar sea contains a small percentage of salt; a red-hot ingot of mild steel holds some two-tenths per cent of carbon, but both the carbon and the salt are in the state of *solid* solution. If the ice had been cooled below −18° C., it would entangle a solidified portion of salt water, which was the last part of the mass to remain fluid. So in the steel ingot, when it has cooled to the ordinary temperature, there is a solidified "mother-liquor" of carburised iron. We do not as yet know whether carbon is dissolved in fluid iron as carbon or as a carbide. We do know, however, that the presence of 0·5 per cent of carbon in iron (such an amount as might occur in a steel rail) lowers the melting-point of the iron from 1600° C. to 1530° C. This lowering has enabled a calculation to be made, the result of which shows that the number of atoms in a molecule of carbon in *fluid* iron at this temperature is probably *two*. It can be shown that at a temperature of 800° C. the number of atoms in the molecule of carbon dissolved is *solid* iron is, in all probability, *three*. At lower temperatures the number of atoms is probably more than three. We metallurgists are not accustomed to think in atoms. Let me, therefore, represent such a three-atom molecule thus:—



without assuming how much iron is associated with the carbon. Following Bergman's experimental method, but with the interval of more than a century separating his work from ours, we investigate the action of acids on carburised iron with a view to ascertain the nature of the atomic grouping of the carbon.

In explaining this I may adopt the appended figure. It is most difficult even to attempt to make questions of atomic grouping clear in a paragraph, but the figure will be helpful. To the historian it suggests vivid pages of Italian history, as the six spheres so arranged constitute the arms of the powerful family of Medici. To the chemist it is a precious symbol, and appeals to him as representing the carbon atoms as grouped in the benzene ring.

The result of treating carburised iron with various acids is the formation of marsh-gas and more complicated organic compounds, of which propylene, acetylene, ethylene, and naphtha may be mentioned. Does the nature of these products help us to ascertain the number of the atoms in the carbon molecule as it exists in cold steel? I have consulted organic chemists, among whom I would specially mention my colleague, Dr. Wynne, and their evidence is encouraging. The result of the action of powerful oxidising agents on certain forms of carbon is mellitic acid, $C_6(CO_2H)_6$, which is one of the benzene series, and this favours the view that solid carbon contains twelve, or some multiple of twelve, atoms in the molecule. But mellitic acid is graphically represented in the annexed diagram, the carbon atoms being arranged



as the six spheres are in the arms of the Medici. The group CO_2H is tacked on to each carbon sphere. From this it may be argued that the molecule of solid carbon consists of one or more carbon "rings." In cold steel the group of CO_2H may be replaced by the group Fe_3, which is broken off by the action of suitable solvents, leaving free carbon. Hence the six-atom carbon molecule may exist in steel.

My object is merely to show you how far at the end of the century we have advanced in our knowledge of the mode of action of carbon, and I trust it will be evident that the progress is remarkable. We know that even in solid iron the carbon atom must push and thrust with great vigour, for we can measure the "osmotic pressure" the carbon atom exerts, and, as has just been shown, we can even picture the mode of the atomic grouping in the molecule.

I can only just sum up the evidence as to the occurrence of molecular change in iron. To Gore, and to Barrett, we owe the investigation of the nature of a fact which had long been well known to smiths, that iron on cooling from a bright red heat suddenly emits a glow. We now know that as steel cools down there may be at least six points at which molecular change occurs, accompanied by evolution of heat.

In a series of classical papers of which we are justly proud, for many of them have been communicated to this Institute, our member, Osmond, has shown what is the significance of some of these points, and has won an enduring reputation. We measure and record them photographically as readily as if they were barometric variations. It is known that three points occur in the purest electro-

iron yet prepared. Two points are connected with the magnetic permeability of iron. One point at least is due to the power iron has of dissolving carbon; two points which occur far below a red heat appear to be due to the presence of hydrogen. Moreover, the molecular condition of steel cooled from an intense white heat is not the same as that of steel which has just been melted. To carry further the evidence as to the effect of an intense heat on iron in a vacuum is the task I have in prospect during my Presidency of the Institute. I may, however, express my agreement with Lockyer's view that the evidence afforded by the atmosphere of the stars shows that our terrestrial iron is a very complex form of matter.

We must not lose sight of those relations of carbon and iron which involve physical equilibrium. Even the astonishing associations of iron and carbonic oxide in the volatile gaseous compound with which the distinguished name of Mond is connected, affords a triumph of dynamic chemistry. It is generally supposed that ozone is dissociated at 160° C., but Dewar has devised a beautiful experiment to prove that ozone has two centres of stability, and one of these is near the melting-point of platinum. It seems to be the same with the relation of hydrogen and iron. We have recently learned that iron and hydrogen appear to be completely dissociated at 800° C., and yet the same iron heated to some higher temperature, say 1200° C., will still yield hydrogen.

Let us suppose that Black, Cort, and Bergman were with us again, and had reviewed the present state of our knowledge and the work accomplished in the century. Let us also suppose that they could go to Sheffield and see an armour-plate rolled and finished for service, and then, visiting our Institute, hear the best explanation we could offer of all the incidental phenomena they had witnessed. Which would they consider the more advanced, our practice or our theory? They would probably hesitate to tell us, but would offer warm congratulations on the immediate prospect of the establishment of a National Physical Laboratory, in which investigations as to the properties of iron and steel will be continued.

Economic Considerations.—The relations subsisting between capital and labour are of vast importance to our industry, and it would not be justifiable to omit reference to them. There is, indeed, abundant precedent for the discussion of this subject in the Presidential Addresses of Mr. Windsor Richards and Sir David Dale.

I venture to hope that the next generation will look back with astonishment to the deplorable aspects presented by what is known as the labour question at the close of the nineteenth century. It is only natural that British enterprise should be met by foreign competition, and I will not dwell on the evidence of our shortcomings in adapting ourselves to the requirements of foreign trade afforded by our "shaming Consular Reports." They are serious enough; but as regards the workmen, their demands for increased wages and reduced hours of work, and, what is far more serious, for the right to determine how little shall be done in those hours, entirely ignore the conditions under which other nations are competing with us. The situation last year was even perilous, for twelve unfinished warships bear eloquent testimony "to the great, though fortunately not irretrievable, misfortunes primarily traceable to the recent engineering dispute."

The multiplied strikes of the last few years have deprived the country of the great advantage it formerly possessed, both as regards excellence of work and punctuality of delivery. To take only the last coal strike; the indictment against the men was thus tersely expressed in *The Times:* "The men lost some £3,000,000 in wages; they crippled the coal trade; they stopped the naval manœuvres; they spread misery broadcast in the district; and they played into the hands of the non-associated owners, who realised large profits, of which but a very small portion found its way into the pockets of the workmen." Capital and labour, which ought to be in amicable association, are too often antagonistic. It may be urged that the antagonism is but a struggle, and that the fittest and strongest must survive, and that we are powerless in the presence of the working of a natural law. Formerly some of us might have been disposed to accept this as inevitable. But my late distinguished colleague, Huxley, in the Romanes Lecture delivered by him at Oxford in 1893, recognised that there are two opposing methods at work in the government of the world. These are respectively the *ethical* and the *cosmic*. The practice of that which is ethically best involves a course of conduct which in all respects is opposed to that which leads to success in the cosmic struggle for existence. "In place of ruthless self-assertion, it demands self-restraint; in place of thrusting aside or treading down all competition, it requires that the individual shall not merely respect, but shall help his fellows; its influence is directed not so much to the survival of the fittest, as to the fitting of as many as possible to survive." Thus Huxley, one of the most acute thinkers of the century, has placed sympathy on a scientific basis by suggesting to us that, in the complex problems which the labour question presents, the ethical method must not be lost sight of; no effort to provide for the well-being of the industrial population can be too persistently adopted. Strangely enough in giving advice to workmen at this critical time, when, as the result of labour conflicts, trade has been lost to the country, we can appeal directly to their self-interest, and in this case industrial influences will be more effective than ethical ones. It is, moreover, through economic means and industrial influences that mankind tends to grow together, and it may confidently be anticipated that the workmen's self-interest, if only it can be rightly directed, will effect the changes in the relation between capital and labour which the moral sense of the men has been unable to accomplish. The highest ethical teaching of true leaders like David Dale, "will then find their late echo in the assent of the multitude."

"Within the trade union movement," write Mr. and Mrs. Sidney Webb in their very interesting work on "The Industrial Democracy," "we find the collectivist-minded working-man grounding his regulation of the conditions of employment upon what we have called the doctrine of a living wage." What that wage should be is most difficult to define; but is there an employer who hears me who is not anxious that each of his people should earn a "living wage," or who feels that the conditions of the life of labourers in the Black Country, as pictured by Charles Dickens in the forties, disgraced humanity? How could people who dwelt under such conditions respect themselves?

How can the legitimate self-interests of the workmen be rightly directed? We must hope that the inclusion of the teaching of economic subjects in the scheme of primary education will do much. We must hope that Boards of arbitration and conciliation will have immediate effect, and will find their full fruition with the rising generation, who may be expected to be more firmly disciplined and to have a higher sense of duty than their fathers. We must trust that frequent discussions between employers and the employed will enable mutual interests to be clearly seen. We must learn that the warmest sympathy with the workmen's rights is not inconsistent, in face of common dangers, with stern and vigorous treatment of labour difficulties which threaten the national prosperity.

Let us hope that advantage will be taken of the prevailing prosperity to place these questions on a satisfactory basis.

Conclusion.—It will have been evident how great a share our country has had in forming the age of steel. The range of properties steel possesses is wide, and by its use the efforts of a multitude of workers have been, as it were, concentrated in a few great efforts which have exerted vast influence on the progress of humanity. Men with most varied aims have, by the use of steel,

been enabled to reveal their genius. Especially is this true of the Members of the great Institution of Civil Engineers, whose hospitality is so generously extended to us. The forces of Nature have been utilised through the intervention of machinery, which could not have been constructed if steel had not been known. By the adoption of steel distance has been abridged, and it has been possible to express our national attributes of courage and endurance in concrete forms. You who produce steel have enabled the designer of the greatest fleet ever seen to claim that our nation has "become the ship-builders of the world."

As a plastic material steel has served as a vehicle for embodying the imagination of the Art Worker. To the Chemist and Physicist steel presents complex problems for research, and affords boundless hope that further changes in its composition or treatment will enable new wonders to be wrought which will make the future a rich inheritance.

At the end of the century we are hoping that a Royal Charter will be granted to our Institute, the members of which have, as I have shown, done so much. That the well-being of the nation depends on its scientific and industrial progress was recognised in the charter given to that centre of all scientific advance, the Royal Society, in 1662, by His Majesty King Charles II. In this charter the King said: "We have long and fully resolved with Ourself to extend not only the boundaries of the Empire, but also the very arts and sciences." The method by which this was to be effected had been suggested long before by the better-known words of another monarch, who wrote the proverb: "It is the glory of God to conceal a thing, but the honour of kings is to search out a matter." Industrial or scientific truths are hidden, but we have freedom of search by "actual experiment." The humblest investigators of the properties of iron and steel may, therefore, make the resolve of Charles II. and share the glory of Solomon; for, bringing our intellectual gifts into closer union with our practical interests, and broadening the boundaries of the metallurgic art, will assuredly enable us to make better use of our existing possessions, and will lead to the extension of the Empire.

NOTICES OF BOOKS.

New York Experimental Station, Geneva, N.Y. Bulletins No. 150—154. Published by the Station, 1898.

During the past two years the raspberry saw-fly has done serious injury in certain localities in the State. Experiments show that the larvæ can be successfully checked by spraying with hellebore (one ounce to a gallon of water). The grape-vine flea-beetle has also been abundant. Experiments with this insect are not yet complete, but the adults have been checked with Paris green (at the rate of one pound to 50 gallons of water, with the addition of enough slaked lime to make the mixture milky in appearance); this should be applied as a fine spray.

Experiments in ringing grape-vines were begun in 1896 and continued during two seasons. The effect on some varieties was very marked, both the bunches and the berries being larger, and ripening beginning earlier. There can be little doubt that the effect of ringing is devitalising to the plant, but when judiciously managed need not result disastrously.

The apple tree tent caterpillar and the canker worm are easily destroyed by Paris green, green arsenite, and arsenite of lime. The two latter have the advantage of cheapness, and will remain suspended in water much longer.

Commercial fertilisers for potatoes have also occupied some attention, the work described in *Bull.* No. 154 being the continuation of the tests made in 1897. The new tests included sixty-four ¼-acre plots on four farms, and were planned to ascertain the effect of a full amount of potash as compared with two-thirds as much, one-third, and none at all. The fertiliser without potash was as efficient as those containing it, so the variations in amount showed no influence.

In the Director's report for the year is given a description of the new Biological and Dairy Building. A number of illustrations show clearly its construction and equipment. It is now two years since the Station began the publication of the so-called popular *Bulletins*, and they are now sending out over 32,000 copies, and the number is still growing. A number of tests were made on growing fruit, vegetables, &c., from foreign sources in carefully prepared soils, but the only really promising one in the whole list proved to be one of the cabbages of the flat Dutch type.

CORRESPONDENCE.

NEW CONDENSER.

To the Editor of the Chemical News.

Sir,—We note in your issue of May 12th (vol. lxxix., p. 217) a description of a new condenser by F. W. Aston.

We beg to advise you that we have been making a condenser, patented by Mr. Cecil H. Cribb, for some months (and that we have the sole rights for making these in glass), and we enclose particulars of same.

From these particulars you will see that, in the condenser which Mr. Aston describes, there is no new idea whatever. Mr. Cribb's patent covers the making of these condensers in any shape, therefore the one described in the paper is an infringement.—We are, &c.,

C. E. Müller & Co.

148, High Holborn, London, W.C.,
May 31, 1899.

COMPOSITION OF MANGANESE PYRO-PHOSPHATE.

To the Editor of the Chemical News.

Sir,—It will be of interest to analytical chemists to call attention to an error in the latest English edition of Fresenius's "Quantitative Analysis" (A. Vacher, 1876, vol. i., p. 133), where pyrophosphate of manganese is stated to consist of 2MnO 35·50 and PO_5 71. This should, of course, be 2MnO 71, and PO_5 71, and the percentage of these respectively 50 and 50.

In the German edition, from which this was translated, no figures are given for the composition of this substance,—hence the error no doubt arose from want of care in filling out that omission.—I am, &c.,

F. P. Dunnington.

University of Virginia,
May 12, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 19, May 8, 1899.

Separation of Traces of Bromine existing in Chlorides.—H. Baubigny.—If a known weight of chloride in the form of a saturated or nearly saturated solution, and very rich in copper sulphate, is treated with perman-

ganate (about one-tenth of the weight of the chloride) in the cold, the whole of the bromine, which the chloride contains in the form of bromide, can be extracted, but at the same time traces of chlorine are also liberated. After this operation, it is sufficient to treat the alkaline liquid from the condenser, where the chlorine and bromine have been collected, at 100° by the ordinary method for chlorine. The liquid contains only minute traces of chlorine, but these can be accurately determined and subtracted from the total result after the first operation.

Impurities of Aluminium.—Adolphe Minet.—The impurities of aluminium prepared by the new electrolytic method consist principally of silicon, iron, and traces of carbon. The exact amounts have been determined for aluminium prepared at different times.

	1890. Per cent.	1893. Per cent.	1897. Per cent.
Silicon	0·90	0·25	0·02
Iron..	0·40	0·40	0·12
Aluminium ..	98·70	99·35	99·86

Phosphide of Magnesium.—Henri Gautier.—The direct combination of magnesium and phosphorus furnishes a phosphide having the formula Mg_3P_2. This compound is decomposed by water very easily, giving magnesium and pure gaseous phosphoretted hydrogen. Its chemical activity is very great; it acts easily on oxygen, chlorine, &c.

The Flame of Hydrogen.—MM. Schlagdenhauffen and Pagel.—Authors generally agree in saying that the hydrogen flame is very pale; but it has been little noticed that the flame is green or blue, according to the purity of the gas. The authors have experimented on this subject, and have arrived at the following conclusions:—(1) The flame of hydrogen, whether pure or impure, becomes decidedly violet-blue when it is pressed down by a cold body, glass or porcelain, with various experimental conditions. (2) This coloration is due, not to the presence of sulphuretted hydrogen, as Salet believed, but to that of seleniuretted hydrogen.

Hydrogenation of Acetylene in presence of Nickel.—Paul Sabatier and J. B. Senderens.—It has already been noticed that nickel in the form of oxide reacts at a low temperature (30° to 45°) on a mixture of equal volumes of ethylene and hydrogen; at 300° it acts on ethylene alone. These results led the authors to investigate the action of hydrogen on acetylene in presence of nickel oxide. They found that nickel serves to produce easily the hydrogenation of acetylene; indeed, that this reaction is produced immediately at a low temperature. It is found that the normal reaction of nickel on acetylene mixed with excess of hydrogen produces ethane, with a slight proportion of ethylene.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., July 25, 1898.

On the Racemics.—F. W. Kuster.—The author has endeavoured to prove that the racemics are stable, not only in the crystalline state, but also in solution. He is of opinion that a combination is effected in the liquid mass.

The Nitroso-derivatives of the Fatty Series (Nitroso-isobutyric and Nitro-isobutyric Nitrites).—O. Piloty.—If the nitrite of amidoxyl-isobutyric acid is treated with an oxidising agent in cold aqueous solution, it is transformed into the corresponding nitroso-derivative, $(CH_3)_2.C\begin{matrix}NO\\CN\end{matrix}$; a white crystalline mass fusible at 53°, forming a deep blue liquid, soluble in alcohol, insoluble in water. This nitroso-derivative decomposes with violence at about 80°. If the action of the oxidising agent is prolonged until the decoloration is complete, we obtain the nitro-derivative, $(CH_3)_2.C\begin{matrix}NO_2\\CN\end{matrix}$, in white prisms, fusible at 35°, soluble in all the organic solvents with the exception of ligroïn, and slightly soluble in water.

The Oxysulphonic Acids and the Sultones.—W. Markwald and H. H. Franne.—The authors have obtained a chlorised product from the action of pentachloride of phosphorus on *o*-benzaldehyde-sulphonic acid, and they propose for it the name *tolyl-sultone*. They have also examined an isomer which they call *benzyl-sultone*. The analogy existing between the chemical properties of the ortho-substituted benzylic derivatives and the corresponding "peri" derivatives of naphthalene lead the authors to believe that *o*-dinitrobenzylsulphonic acid ought, by analogy with peridinitronaphthalene sulphonic acid, to give benzylsultone, $C_6H_4\begin{matrix}CH_2\\O\end{matrix}\!>SO_2$. Experiment has shown this view to be correct.

Synthesis of Phenanthrene and the Hydrogen Derivatives of Phenanthrene by means of α-Naphthoic Acid.—P. Rabe.—When an alcoholic solution of one molecule of acetacetic-sodium ether and one molecule of the ether of Δ'-dihydro-α-naphthoic acid is boiled, the acetacetic ether joins, in the first phase of the reaction, with the double bands of the second ether, giving a δ-ketonic ether. But under the condensing influence of the ethylate of sodium, a closing of the nucleus takes place with the formation of the ether of 1:3-diceto-octohydrophenanthrenecarbonic acid. This ether, by elimination of the carboxy-ethylic group, easily gives 1:3-diceto-octohydrophenanthrene, a strong monobasic acid which may be regarded as an unsaturated oxy-ketone.

MEETINGS FOR THE WEEK.

THURSDAY, 15th.—Chemical, 8. Ballot for the Election of Fellows. "On the Decomposition of Chlorates, with special reference to the Evolution of Chlorine and Oxygen," by W. H. Sodeau, B.Sc. "The Action of Hydrogen Peroxide on Formaldehyde," by A. Harden, M.Sc., Ph.D. "Homocamphoronic and Camphononic Acids," by A. Lapworth and E. M. Chapman. "Action of Silver Compounds on α-Dibromocamphor," by A. Lapworth. "The Colouring-matter of Cotton Flowers," by A. G. Perkin. "Experiments on the Synthesis of Camphoric Acid," by H. A. Auden, W. H. Perkin, jun., and J. L. Rose. "Methylisoamylsuccinic Acid" (Part I.), by W. T. Lawrence.

INSTRUCTION IN
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Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896). Alfred Jörgensen, "Micro-Organisms and Fermentation," London (F. W. Lyon), 1893.

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Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2064.

A CONTRIBUTION TO THE STUDY OF INVERTINE.

By W. A. OSBORNE, M.B.

That yeast contains a substance acting hydrolytically upon cane-sugar was first discovered by Baudrimont and Dubrunfaut (*Journ. f. Prakt. Chemie*, xiv., 334). Liebig (*Ann. Chem. Pharm.*, cliii., p. 1) pointed out that this constituent of the yeast could be precipitated from a watery extract by basic acetate of lead. Hoppe-Seyler (*Ber. d. Deutsch. Chem. Gesell.*, iv., 810), though, was the first to make any serious attempt to isolate this ferment. Yeast was rubbed up in a mortar with ether, and then an aqueous extract made which possessed invertive properties. Berthelot (*Comptes Rendus*, vol. l., p. 980) made a watery extract of yeast from which the ferment was precipitated by alcohol. Gunning (*Ber. d. Deutsch. Chem. Gesell.*, v., 821) extracted yeast with glycerin, and used alcohol as a precipitant. Donath (*Ber. d. Deutsch. Chem. Gesell.*, viii., 795) first gave the name invertine to this enzyme. Adopting the method of Zulkowski and König, he treated the yeast first with alcohol, filtered off the alcohol and allowed to dry. A watery extract was then made of the yeast, which when shaken with ether gave a gelatinous mass. This latter, when allowed to drop in to excess of alcohol, gave a white flocculent precipitate of invertine.

Barth (*Ber. d. Deutsch. Chem. Gesell.*, 1878, p. 118) devised a method of preparing invertine which still continues in use. Yeast was allowed to dry thoroughly at a temperature below 40° C.; it was then subjected to a temperature of 100—105° C. for several hours. A watery extract was then made which, when dropped into excess of alcohol, gave a rich precipitate of the ferment.

The first object of the present research was to select or devise a method of preparing a crude invertine which should have its enzymotic qualities as strong as possible, and which might serve as a basis for further research. For this purpose the following preparations were made:—

A. Half a kilo. of yeast was rubbed up with 500 c.c. 96 per cent alcohol and allowed to stand over night. The alcohol was then filtered off and the residue spread out on a filter-paper and allowed to dry in sunlight. When dry and brittle, it was rubbed up with 300 c.c. chloroform water (5 in 1000) and allowed to stand six days at a temperature of 35° C. At the end of this time the mixture was filtered, and the filtrate dropped into tall cylindrical vessels three-quarters full of 96 per cent alcohol. The precipitate formed was collected, washed once with absolute alcohol, and dried over H_2SO_4 *in vacuo*.

B. In this case the ferment was prepared in the same way as A, with this exception—that the yeast was extracted with water without any previous treatment with alcohol.

C. This invertine was prepared after the recipe of Barth. The extraction was made with chloroform water and lasted six days.

D. As with C, only that in this case the yeast was dehydrated with alcohol before being subjected to the high temperature.

To test the invertive powers of these preparations, an estimation was first made of the percentage amount of soluble matter in each. A solution was then made of each in water containing 2 per cent of soluble matter. Two c.c. of this solution were added in each case to 20 c.c. of a 1 per cent cane-sugar solution in a test-tube, which was then placed in a water-bath at a temperature of 35° C. At the end of half an hour the mixture was boiled and then transferred to a burette. The amount of invert sugar was tested in the usual way by Fehling's solution, using 5 c.c. of the latter.

The accompanying table gives a comparison of results, each being the average of six experiments. It will be seen from this table that invertine A possesses a high degree of solubility, whilst its invertive properties are strong and constant. It was therefore chosen as a starting-point for further research—Invertine I.

A solution of Invertine I. does not coagulate on boiling, and gives no precipitate on saturation with metallic salts or ammonium sulphate, nor on addition of mercuric chloride or ferrocyanide of potassium with acetic acid.* Proteid impurity may therefore be considered absent. The principal impurities are inorganic in nature, amounting sometimes to nearly 50 per cent of the whole. To remove these, Barth had no other method to propose than to dissolve the ferment in water and precipitate with alcohol, and to repeat this process indefinitely. He confessed, however, that the invertine lost more and more of its active properties when subjected to this treatment, and we are thus confronted with the paradox that the purer the ferment is, the weaker it acts. To explain this loss of invertive power, it has been suggested, on the one hand, that alcohol acts injuriously; and, on the other, that the inorganic ingredients belong to the actual molecule of the ferment. It will be seen from the following researches that the greater part of this inorganic matter may be removed without in any way reducing the active properties of the invertine.

A preliminary clue to the nature of these inorganic impurities may be obtained by a consideration of the constitution of the ash left behind on calcining yeast. According to Belohoubek (quoted in "Die Hefe," by Dr. Edmond Kayser, German edition, 1898), this ash contains—

	Per cent.
Phosphoric acid	51·1
Sulphuric acid	0·57
Silicon dioxide	1·60
Chlorine	0·03
Potassium	38·68
Sodium	1·82
Magnesium	4·16
Calcium	1·99
Other substances	0·06

* Zinc sulphate gives a precipitate of phosphates, but this does not occur if the solution be previously acidified.

Invertine.	Yeast.	Invertine obtained: Grms.	Solubility in water.	Starch solution.	Invertine solution.	Time and temperature.	Amount of Inverted solution necessary to reduce 5 c.c. Fehling.
A	Kilo.	5·7	96 per cent	20 c.c. of a 1 per cent solution.	2 c.c. of a 1 per cent solution.	Half hour at 35° C.	3—3½ c.c.
B	Kilo.	17	About 75 per cent.	20 c.c. of a 1 per cent solution.	2 c.c. of a 1 per cent solution.	Half hour at 35° C.	3 c.c.
C	Kilo.	6—8	95—96	20 c.c. of a 1 per cent solution.	2 c.c. of a 1 per cent solution.	Half hour at 35° C.	5—9 c.c.
D	Kilo.	6—8	97	20 c.c. of a 1 per cent solution.	2 c.c. of a 1 per cent solution.	Half hour at 35° C.	∞ (inert).

Magnesium and potassium phosphate are therefore amongst the most likely components of the mineral element in invertine.

The insoluble residue left behind on dissolving invertine proved to consist chiefly of magnesium phosphate with a slight amount of iron and a certain admixture of organic matter.

If now to the filtrate ammonia be added a fairly heavy precipitate of NH_4MgPO_4 falls.* Being crystalline this precipitate does not enclose any of the ferment in its substance, as is the rule with phosphatic precipitates in general. The filtrate from this precipitate may now be placed *in vacuo* over H_2SO_4, in order to remove NH_3 and water. The ferment so obtained is a brown, resinous, and somewhat hygroscopic mass, readily soluble in water, and possessing strong invertine powers = Invertine II. Ammonia, even in strong excess, seems to exert no injurious action on invertine. To test the comparative strengths of I. and II., 1 c.c. of a 1 per cent solution of each was added to 20 c.c. of a 1 per cent cane-sugar solution, and placed in a water-bath at 35° C. for five minutes. At the end of this time the mixture was boiled and placed in a burette. An estimation was then made of the amount necessary to reduce 5 c.c. Fehling.

I. = 12 c.c.
II. = 11½ ,,

It thus appears that II. is actually stronger than I., which is explained by the fact that in the former there is a higher percentage of actual ferment. It might further be mentioned in this connection, that a strong solution of Invertine II. possessed invertine powers as strong as those just given after lying some years under a bell jar, containing also a small vessel half-full of H_2SO_4, all traces of NH_3 having disappeared.

The proportion of the magnesic phosphate to the remaining mineral impurity may be judged by the two following ash analyses:—

	1.	2.
Invertine I.	44·58	31·62
,, II.	29·3	19·96

About a third, therefore, of the total inorganic impurity is removed by the simple process of treating with NH_3.

As a further step in the process of preparing a pure ferment, a substance was sought for which could form with the invertine an insoluble combination from which the ferment might afterwards be separated.

Potassio-mercuric iodide, which, according to Wroblewski (*Zeitsch. f. Physiol. Chemie*, xxiv., 173), acts so well with diastase, gives no precipitate with invertine. On the other hand, phospho-tungstic acid, in presence of a mineral acid, is a true precipitant. To determine beforehand to what degree mineral acids are injurious to the invertine, the following experiments were made:—

A number of test-tubes were taken, each containing 10 c.c. of a 1 per cent solution of II. To each was added 10 c.c. of dilute acid in varying strengths. The test-tubes were placed in a water-bath at 35° C., and kept there over night. On the following morning the contents of each were neutralised by the corresponding amounts of normal sodium hydrate solution; a few c.c. of cane-sugar solution were added, and the test-tubes placed again in the water-bath for half-an-hour, at the end of which time invert-sugar was tested for by Fehling.

	Strength of acid in a 0·5 solution of II.	Invertine power.
(*a*). HCl ..	1/24 normal	Completely destroyed.
	1/36 ,,	Almost completely destroyed.
	1/40 ,,	Slightly lessened.
	1/48 ,,	Not appreciably lessened.
(*b*). H_2SO_4	1/20 normal	Completely destroyed.
	1/24 ,,	Almost completely destroyed.
	1/36 ,,	Very slightly or not at all lessened.

* Any commercial invertine will give this precipitate with NH_3.

Seeing how readily the invertine is affected by mineral acids, the prospect of success with the phospho-tungstic method is not very great. An attempt, however, to use this method was made, dilute H_2SO_4 being added drop by drop along with the phospho-tungstic solution, whilst the mixture was vigorously stirred. The precipitate was washed with dilute H_2SO_4, treated with $Ba(OH)_2$ and CO_2, but no active ferment could be obtained. Most probably the phospho-tungstic acid is itself injurious to the invertine.

In the next experiments neutral lead acetate was employed. It was found, in preliminary experiments, that to obtain an active ferment the phosphates must first be removed from II. For this purpose either $Ba(NO_3)_2$, with a little NH_3, was added to the solution, or, as the barium phosphate brings down a quantity of ferment, $Mg(NO_3)_2$ and NH_3.

To the filtrate neutral lead acetate solution,* with a little NH_3 was added until no more precipitate formed. The whole was then filtered, and the precipitate washed thoroughly until the wash water was free from nitrates, as proved by the diphenylamine test. The precipitate was then suspended in water, and a stream of H_2S passed through until the colour was uniformly black. The mixture was then filtered, and the filtrate allowed to evaporate at a temperature of 35° C. in a strong current of air.

The great difficulty with this method was to prevent lead sulphide appearing in the final filtrate; acid, as we have seen, could not be added at any stage of the process. In one of the most successful attempts with this method, a clear glassy substance was obtained, faint brown in colour, strongly invertive in property, and containing 4·54 per cent ash.

As the difficulties connected with the semi-solubility of PbS were too great to overcome completely, it was decided to discard this method for the time being, and to try the effect of prolonged dialysis. Accordingly a solution of II. was made, and dialysed for several weeks in an apparatus slightly modified from that described by Wroblewsks (*Zeits. f. Phys. Chem.*, xxiv., 173), chloroform being constantly added to the water. Though the dialysing tubes were carefully tested, it was found that the water in the dialysor possessed invertive powers, a small quantity of the ferment having evidently penetrated through the parchment-paper. The contents of the tube were finally taken out, filtered, if necessary, from any slight sediment which had formed, and evaporated in a strong current of air at a temperature of 35° C. = Invertine III.

In every case the substance thus obtained was strongly invertine, and contained inorganic impurity to a comparatively slight degree, as proved by the following ash analyses:—

	1.	2.	3.	4.
Ash analysis ..	1·83	2·24	1·72	1·61 per cent

As, however, dialysis carried out in this manner is a rather tedious process, some improvements were made in order to shorten and facilitate the method. In the first place, phosphates were removed by adding to the solution of II. a slight excess of ordinary laboratory magnesian mixture. The filtrate from this was then dialysed. By means of a double crank arrangement, worked by a small water motor, an alternating up-and-down movement was given to both ends of the parchment tube. By this means both invertine solution and the surrounding water were kept in a continual state of motion. Chloroform was added to both water and solution. When, on testing a small portion of the solution no precipitate was obtained with either $AgNO_3$ or $BaCl_2$, the contents of the tube were taken out, filtered by means of a Pukall filter, and evaporated by boiling *in vacuo*. The temperature remained below 30° C. throughout this latter process, so that the ferment was not in any way injured. When a syrupy consistence had been reached, the ferment was

* I could never succeed in preparing an active ferment by using the basic solution.

precipitated by addition of excess of alcohol and ether. It was then washed with absolute alcohol and dried *in vacuo* = Invertine IV. Thus prepared, invertine is an extremely light powder, of whitish-grey colour, readily soluble in water, and possessing invertive powers of a high order. As regards inorganic matter, the least obtained on ash analysis was 1·83 per cent.

Constitution of Invertine.

That the large percentage of inorganic matter in ordinary invertine is not a necessary component of the ferment may be deduced from the foregoing facts, namely, that these inorganic constituents may be reduced 90 per cent without making any appreciable diminution of the invertive power.

As regards the classification of invertine amongst organic substances, and specially as regards its relation to albuminous bodies, the following reactions with proteid tests may first be given:—

A. Precipitation tests.
1. Coagulation by boiling = negative.
2. Mineral acids, including metaphosphoric = negative.
3. Metallic salts. *a*. Copper sulphate = positive (faint).
b. Lead acetate = positive.
c. Mercuric chloride = negative.
4. Acetic acid and ferro- or ferricyanide of potassium = negative.
5. Saturation with neutral salts, Na_2SO_4, &c., after acidulation = negative.
6. Saturation with ammonium sulphate = negative.
7. Alcohol = positive.
8. Mineral acid and phospho-tungstic or phosphomolybdic acid = positive.
9. Acetic and tannic acids = negative.
10. Potassio-mercuric iodide with HCl (or potassio-bismuth iodide) = negative.
11. Acetic and picric acids = negative.
12. Trichloracetic acid = negative.

B. Colour reactions.
1. Millon's reagent = faint.
2. Xanthoprotein = positive.
3. Adamkiewicz = negative.
4. Buiret = faint.
5. Liebermann's reaction = negative.
6. H_2SO_4 and sugar = negative.

From these reactions it will at once be seen that invertine cannot be classified amongst the ordinary proteids; the possibility, too, of its being allied to peptone, with which it has certain physical properties in common, must also be excluded.

The question may be raised whether the invertine thus prepared is not an admixture of a small amount of active ferment with a relatively large quantity of carbohydrate. To this the answer may be given that its extreme solubility excludes a great many of the carbohydrates; further, that though it indeed gives the Molisch reaction, it does not reduce Fehling; and glycogen, the most likely carbohydrate impurity to be present, is proved absent by the iodine test. The best proof, though, that invertine may be isolated in a comparatively pure condition, is furnished by analysis.

Donath obtained the following percentage composition of invertine:—

C = 40·48 per cent		40·53 per cent
H = 6·88 ,,		6·38 ,,
N = 9·47 ,,		9·36 ,,

Barth obtained the following:—

C = 44·20 per cent		44·60 per cent
H = 8·50 ,,		8·30 ,,
N = 6·40 ,,		5·50 ,,
S = 0·63 ,,		—

These results certainly do not corrrespond well with each other—a sure proof that the ferment in one or both cases was mixed with some other substance.

The following are the analyses obtained in the present research. In all cases the substance was dried in a toluol bath in an atmosphere of hydrogen. A special ash analysis was also made in most cases.

Invertine III.

	1.	2.	3.	4.
Ash	1·83	2·24	1·72	8·22
*C..	45·1	44·3	44·86	45·07
H	6·69	6·5	6·56	6·46

Invertine IV.

	1.	2.	3.
Ash	5·5	5·17	6·78
C	44·05	44·81	—
H	6·54	6·31	—
N	6·03	5·7	6·58

Invertine prepared by Lead Acetate Method.

	1.	2.	3.	4.
Ash..	8·16	10·59	4·54	11·63
C	42·42	42·13	43·89	44·28
H	6·55	6·55	7·45	6·95

As regards the lead acetate method it was found that in the first two cases the lead present in the invertine had formed with the other ash constituents a glassy substance which enclosed a few particles of charred invertine. The hydrogen values may be taken, though, as correct. In the latter two cases the combustion with oxygen stream was continued for a much longer time. This will possibly account for the high values of H, but C may be taken as approximately correct, as the ash was clear and devoid of carbon particles.

The following may be regarded, therefore, as the average percentage composition of invertine:—

C	44·54
H	6·52
N	6·1

That the values for C and H seould remain constant, notwithstanding the different methods of preparation, shows that the invertine was present in a state comparatively pure.

The low percentage of carbon places invertine altogether apart from the proteids.

On the other hand, a distinct similarity may be observed between the percentage composition of invertine and that of chitin, taking Schmiedeberg's formula for the latter (*Arch. für Exper. Pathol. u. Pharm.* xxviii., 41):—

Chitin, $C_{18}H_{30}N_2O_2$ =	C = 46·35
	H = 6·44
	N = 6·01

It is therefore possible that invertine belongs to a class of bodies resembling chitin in chemical structure, amongst which Fraenckel's albamin (*Wiener Sitzungsberichte*, cvii., Abt. II.*b*, p. 819) might also be classified.

Chitin when boiled with HCl gives, as Ledderhose (*Zeit. f. Phys. Chem.*, vols. ii. and iv.) discovered, acetic acid and glucosamine chloride. Experiments made with Invertine IV. showed that HCl, strong or slightly dilute, gives a reducing substance after a few minutes boiling. If the hydrochloric acid be now removed with silver oxide, the solution remains strongly acid, pointing to the probability that some other acid has also been formed. Boiling with HCl produces, if long continued, a black carbon deposit.

This reducing solution, when treated with phenylhydrazine and acetic acid gave, after half an hour in the water-bath, a mass of yellow crystals in rosettes and

* In all these analyses C and H are of course reckoned for the ash-free substance.

sheaves, which, when washed with acetone and re-crystallised in dilute alcohol, had a melting-point of 198° C. (phenylglucosazone 205° C.) and contained 15·5 per cent nitrogen (phenylglucosazone 15·6 per cent).

Unfortunately the amount of Invertine IV. at disposal was not sufficient to make any thorough investigation of this reducing substance. The author soon hopes, however, to complete this part of the research.

The above research was made in the Physiologisch-chemisches Institut in Tübingen, under the guidance of Professor Hüfner, to whom the author is very especially indebted, not only for the suggestion of the research and advice in carrying it out, but also for a large amount of material which was generously placed at his disposal.

NOTES ON THE ELECTRO-DEPOSITION OF PALLADIUM.*

By SHERARD COWPER-COLES, M.Inst.M.M.

PALLADIUM is usually found associated with platinum, and as a rule it does not exceed 1 per cent. It is generally separated from platinum by chemical processes.

At the present time the uses for palladium are very limited, the demand being considerably less than the supply, consequently the price is low as compared with some other rare metals. The present price is about double that of platinum, but its specific gravity is about half. Its colour is almost as white as that of silver, and it takes a beautiful polish. Palladium is very malleable and ductile, and is harder than platinum. The following table gives the hardness of electro-deposited palladium as compared to other metals:—

Nickel electro-deposited	10·0
Sheffield plate	10·0
Antimony electro-deposited	9·0
Palladium deposited bright..	8·0
Cadmium deposited bright	4·5
Silver electro-deposited and burnished	4·0

The figures give the hardness as represented by the number of grms. weight on a diamond point required to produce a scratch.

Palladium fuses at a somewhat higher temperature than platinum. Moissan has found that palladium, like platinum, dissolves carbon at the temperature of the electric furnace, but does not unite with it, the whole of the carbon separating out as graphite on cooling.

The author has recently used palladium as a protective coating and reflecting surface for parabolic reflectors, some specimens of which are on the table, the whole of the parabolic reflector being made by electro-deposition. The palladium can be deposited quite bright on the surface of the mirror, so that it does not need polishing, which would destroy the true parabolic curve. A deposit of 70 to 80 grains per superficial foot is found to afford a good protective coating. Such a film of palladium is probably transparent, in which case a considerable portion of light would be reflected from the silver surface beneath the protective film of palladium.

Palladium is unchanged by air at ordinary temperatures, but at a moderately high temperature a thin film of oxide is formed which has a bluish colour. At a higher temperature the oxide is decomposed. Palladium alloyed with one-tenth silver is sometimes employed for the graduated scales of astronomical instruments.

Smee devoted some attention to the electro-deposition of palladium, and attempted to deposit metallic palladium from the nitrate, but only succeeded in getting down a black powder. He found ammonio-muriate of palladium dissolved in ammonia to be the best. He also tried iodide of palladium, by adding a solution of iodide of potassium to a solution of palladium, but found it was not a suitable salt for electro-deposition. He also tried palladio-cyanide of potassium. An electrolyte made up of cyanide of potassium is said to take up a considerable quantity of metal and yield the metal freely, so that heavy, reguline deposits can be obtained.

Bertrand has succeeded in obtaining good deposits with a solution formed of the double chloride of palladium and ammonium, made perfectly neutral; a palladium anode was found to dissolve freely.

Gore has electrolysed a solution of chloride of palladium, in which a palladium anode was found to dissolve, and a black deposit of palladium was obtained upon the cathode.

The author has found a solution of palladium ammonium chloride to be one of the best, if not the best, for depositing palladium in a bright form, such as exhibited here to-night. The best proportions are about a 0 62 per cent solution of palladium ammonium chloride dissolved in about a 1 per cent solution of palladium ammonium chloride. The solution is worked at a temperature of about 75° F., the current used per sq. ft. being about 0·12 ampère, the E.M.F. at the terminals of the bath being 4 to 5 volts. The anodes can be either palladium foil or carbon.

* Read before the Institution of Mining and Metallurgy.

THE ESTIMATION OF SULPHUR AND SULPHATE OF COPPER IN ANTIPHYLLOXERIC MIXTURES.

By Dr. G. SCARLATA.

THE mixture of sulphur and sulphate of copper, employed now for combatting the diseases of the vine, is the object of numerous falsifications, resulting from speculation and mutual agreement between makers. It is therefore useful to have a simple and rapid method of verifying the composition of these mixtures.

The method now generally in use is quickly performed, but from the point of view of accuracy it leaves much to be desired. It is based on the extraction of the sulphur by sulphide of carbon. Now we know that this extraction may be incomplete if the sample contains the insoluble variety of sulphur.

In the same way, the volumetric titration of the copper does not give absolute certainty, and in analyses done sometimes by inexperienced chemists, the results depend more or less on the particular conditions in which the operator is placed.

I may add that, at the present day, *makers* find means, by suitable additions, to falsify the results of the colorimetric titration of the copper, and prevent the complete extraction of the sulphate of copper by water, except when the water is acidulated.

Having had considerable experience in this class of analysis, I am quite satisfied of the small amount of confidence which should be placed in the methods now used, and I have therefore endeavoured to unite all the conditions necessary for accuracy and rapidity.

My process is based on the two following principles:—

1. The sulphur can be determined by oxidation and titration of the sulphuric acid formed.
2. The sulphate of copper can be determined by the estimation of the sulphuric acid set at liberty by decomposing the sulphate of copper by sulphuretted hydrogen.

The following are the details of manipulation:—Treat 1 grm. of the sample with water acidulated with nitric acid, filter, and wash the residue, which serves for the estimation of the sulphur. This residue is placed in a flask with a round bottom and a long neck, and an excess of fuming nitric acid is added. Heat until the oxidation is complete, pour the liquid into a porcelain crucible, rinse the flask with water, and evaporate the whole on a water-

bath until the nitric acid is completely eliminated. Take up with cold water, and titrate the sulphuric acid with soda or potash.

To estimate the sulphate of copper, heat 10 grms. of the sample in a crucible placed on a piece of asbestos card, until the sulphur is completely eliminated by volatilisation and combustion. Add sulphuric acid, and heat until white fumes cease coming off. Take up with water and treat the solution with sulphuretted hydrogen, filter off the sulphide of copper, wash with water containing a little sulphuretted hydrogen, collect all the wash waters and boil to drive off the sulphuretted hydrogen, and titrate the sulphuric acid with soda or potash.

I have tested this method with a known mixture containing 3 per cent of sulphate of copper, and obtained the following results:—

Sulphur	96·5 per cent.
Sulphate of copper.. ..	2·9 „

This method, as can be seen, has a degree of accuracy quite sufficient for practical commercial work.

It does not require any special apparatus, and is limited to two titrations of sulphuric acid, which can be effected with the same solution of caustic soda or potash.—*Moniteur Scientifique*, Series 4, xiii. (Part I.), June, 1899.

ON CRYSTALLISED TUNGSTEN.

By L. A. HALLOPEAU.

In a previous paper (*Bull. Soc. Chim.*, Series 3, xix., 997) I have shown that the electrolysis of paratungstate of lithium, by means of platinum electrodes, enables us to obtain crystallised tungsten mixed with a certain quantity of platinum. I have repeated this experiment, slightly prolonging the duration or the electrolysis, and using a current of slightly lower intensity (2·6 ampères and 15 volts; the melted mass was cooled as slowly as possible, then heated successively with water, hydrochloric acid, and lithia, as I have already described. Under these conditions we can obtain needles of tungsten reaching up to 4 m. in length, and which can be isolated in a state of purity by picking them one by one. Their analysis has given me:—Tungsten = 99·64 per cent.

It is in this manner easy to prepare, by the electrolysis of paratungstate of lithium, a small quantity of pure lithium crystallised in very good needles.

These crystals have a grey metallic lustre, like that of steel; they are not magnetic.

When heated to redness in a current of hydrogen, tungsten burns, and is transformed into tungstic acid. This tungstic acid is absolutely pure, and retains the form of the crystals of tungsten.

I have also noted the production of crystallised tungstic acid by the combustion in oxygen of crystallised binoxide of tungsten, the preparation of which I have already described in a previous paper (*Bull. Soc. Chim.*, Series 3, xix., 746).

These facts are analogous to that which is observed whenever tungstic acid is prepared by the calcination of a crystallised tungstate of ammonia; the acid obtained appeared also to be crystallised.

The electrolysis of paratungstate of lithium with iridio-platinum electrodes did not give me good results. As a matter of fact, the oxygen given off at the positive pole forms, with this latter, binoxide of iridium. After treating the product of the electrolysis with water, hydrochloric acid, and lithia, there remain prismatic crystals of a deep blue colour, containing iridium and very rich in tungstic acid. This body thus seems to be a compound of tungstic acid and binoxide of iridium; it is mixed with a small quantity of crystallised tungsten and a little platinum.—*Bull. Soc. Chim.*, Series 3, xxi., No. 6.

THE DETERMINATION OF POTASH AS PERCHLORATE.*

By F. S. SHIVER.

(Concluded from p. 271).

Preparation of Perchloric Acid.

As perchloric acid is not a regular article of commerce, it becomes necessary for each one desiring it to make his own supply. There may be mentioned briefly four methods for its preparation, and the literature in which detailed directions may be found.

The Method as Proposed by Schlœsing.—Prepare first potassium perchlorate from potassium chlorate by heating in the usual way. The mass, after the decomposition of the chlorate is treated with boiling water, and then rapidly cooled; the crystals of potassium perchlorate separate; the potassium chloride remains in solution with some of the perchlorate also. The perchlorate is then dissolved and treated with sufficient quantity of hydrofluosilicic acid to obtain the potassium fluosilicate, the perchloric acid being liberated. After standing a while, the precipitate is filtered off, and the filtered solution containing the perchloric acid is concentrated and treated with ammonia. The ammonia salt is next decomposed by hydrochloric and nitric acids, and the solution then evaporated on a water-bath to a syrupy consistency.

The solution is left in this condition for a day or two, to separate further any crystals of potassium perchlorate it may contain. The supernatant liquid is then ready for use after a blank experiment has been conducted with the same.

Process of Perrey.—Perrey has sought to avoid completely the presence of potash in the reagent. He makes use of the principle recognised first by Sérullas that chloric acid, distilled, furnishes a third of its weight of perchloric acid. Barium chlorate, a salt easily prepared, is dissolved in water, and the solution precipitated with sulphuric acid, leaving the chlorate, however, in slight excess. After filtration, the solution is concentrated and distilled, the distillate being collected for use as soon as white vapours show themselves in the body of the retort.

The product which one receives is contaminated with a little chloric acid and chlorine, which can be expelled on the water-bath. The yield of perchloric acid is about the same as in the Schlœsing process.

For details of these two processes consult Grandeau, "Traité d'Analyse des Matières Agricoles," i., 88—91.

Caspari's Method.—This method is quite similar in principle to the method described by Schlœsing. Potassium chlorate is used as a basis, potassium perchlorate being prepared from it in the usual way. The potassium perchlorate dissolved in water is then treated with hydrofluosilicic acid at the boiling temperature, the reaction being as follows:—

$$2KClO_4 + H_2SiF_6 = K_2SiF_6 + 2HClO_4.$$

The solution is then filtered on an asbestos filter under pressure, the clear filtrate evaporated on a steam-bath to small bulk, and allowed to stand for twenty-four hours, whereby is effected the separation of any remaining potassium fluosilicate or perchlorate. It is again filtered and diluted with an equal quantity of water, and barium chloride added in slight excess to remove last traces of sulphuric acid and hydrofluosilicic acid. The clear supernatant liquid is then poured off and evaporated on a water-bath till white fumes of perchloric acid appear.

The solution is then, after allowing any potassium perchlorate that may be present to separate again, diluted with water, and the excess of barium salt most carefully removed with sulphuric acid. The solution is allowed to stand for several days, then filtered through paper, and is ready for use.

* *Journal of the American Chemical Society*, xxi., No. 1.

For details of the process consult Wiley's "Agricultural Analysis," ii., 290, and *Zeit. Angew. Chem.*, 1898, p. 68.

Kreider's Method.—By far the most simple and rapid of all the methods proposed for the preparation of perchloric acid is that worked out by Kreider. The method depends upon the production of sodium perchlorate from sodium chlorate by heating, in the usual way, the subsequent decomposition of the sodium perchlorate by hydrochloric acid with the liberation of perchloric acid, and the precipitation of sodium chloride, which is separated by decantation or filtration. The filtered solution is concentrated on a water-bath till white fumes of perchloric acid appear, then cooled and diluted with water when it is ready for use.

It is manifest that the acid thus prepared is not chemically pure, since sodium chloride is not absolutely insoluble in hydrochloric acid, but if a portion of the acid prepared as above be tested with silver nitrate it will be readily seen that any sodium chloride which may have remained in solution has been converted into perchlorate. Furthermore, unless the sodium chlorate used contained some potassium, or on evaporation the acid was exposed to fumes of ammonia, the residue from the evaporation of a portion of the acid prepared as above will be entirely soluble in alcohol, and the presence of any sodium perchlorate is therefore entirely unobjectionable.

I have, in the course of my work on this subject, prepared the acid by this method several times, and have always found the process very satisfactory, requiring but little time and attention. In my work, however, I found, as the result of blank determination on the acid thus prepared, a very small residue insoluble in alcohol, for which in all cases corrections were made. This correction was very slight, and in no way condemns the process, since it is a very simple matter to determine it once for all on any lot of acid, and make the proper use of the same in the actual determination.

For detail of the process consult Kreider's article in the *American Journal of Science*, xlix., 445—446.

A CONVENIENT METHOD FOR MAINTAINING REDUCTION OF FERROUS SOLUTIONS.

By WILLIAM S. MYERS.

My reasons for calling attention to this method for maintaining reduction in ferrous solutions are, that it is economical, convenient, and effective, and (so far as I have been able to ascertain) new, in this particular application.

Various methods have been used to keep ferrous solutions reduced, such as the introduction of zinc and sulphuric acid, and the addition of syrups, gums, sulphurous acid, or sulphuric acid. These are either unnecessarily expensive or ineffective, as they may interfere with the uses of pure ferrous solutions, and I have not been able to obtain as satisfactory and permanent results with them as with the method which I have made the subject of this note, namely, the addition of 10 per cent of concentrated sulphuric acid and a suitable amount of iron, in the form of small wrought-iron nails, to a 10 per cent solution of ferrous sulphate. The acid under these conditions liberates hydrogen very slowly, and yet fast enough to nullify the oxidising action of the air, even when the solution is exposed in an open beaker.

I have found that ferrous solutions thus made up will keep for more than a month in a practically unchanged condition, while solutions made up with syrups, gums, or with free acids, and similarly exposed, were very largely ferric at the end of the period, and acidified ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4+6H_2O$, was in very little better condition.

When one requires a large amount of ferrous sulphate for qualitative class-room work, for example, an open beaker full of the reagent always in good condition is very useful in saving time, and is of great convenience, and in these respects has been so satisfactory to me that I venture to present the method to the members of the Society.—*Journal of the American Chemical Society*, vol. xxi., No. 1.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 1st, 1899.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MESSRS. S. Wellington, P. J. D. Fielding, C. R. Darling, and H. M. Read were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Dick Dougall, Millom, Cumberland; Ernest Frederick Stephen Lange, Sunny Nook, Victoria Road, Withington, Manchester.

In response to an invitation from the University of Cambridge, the President was delegated by the Council to represent the Society at the Jubilee of Professor Sir G. G. Stokes, and in its name to present the following Address:—

To Sir GEORGE GABRIEL STOKES, Bart., M.A., D.C.L., LL.D., D.Sc., F.R.S.

We, the undersigned, President and Officers of the Chemical Society, beg, on behalf of the Council and Fellows, to offer you our sincere and hearty felicitations on the occasion of your Jubilee as Lucasian Professor of Mathematics in the University of Cambridge.

The fifty years during which you have held a position so honourable in the ancient University which claims you as among the most distinguished of her sons have witnessed an extraordinary and unprecedented development in those branches of natural knowledge which are immediately connected with the work of your professorship. To this development your own labours as a teacher and an investigator have contributed in no small degree. You have profoundly influenced the teaching of physics wherever this subject is taught, and this influence has of necessity extended into those departments of Chemical Science which are directly dependent upon, or are associated with, physics. We gratefully acknowledge the services you have rendered to chemical physics by your researches on hydrodynamics, by your contributions to the theory and practice of spectrum analysis, and by your optical investigations. Your memorable contribution to our own *Journal*, "On the Application of the Optical Properties of Bodies to the Detection and Discrimination of Organic Substances," made more than a third of a century ago, has borne fruit an hundredfold, and to-day the refractometer and the spectroscope are as indispensable to the chemist as is his balance. We are glad to recognise that your interest in our special field of inquiry, springing from that catholicity which is your characteristic, has in no wise abated, for there is hardly a chemical subject bordering upon those branches of physical research which you have made more especially your own that has not been elucidated and benefited by your kindly criticism and advice. There are many workers in our Society who thankfully acknowledge the ready help which you have rendered to them by your counsel and suggestions.

That you may long continue to enjoy, in health and prosperity, the esteem and respect with which you are universally held by those who labour for the advancement of knowledge and the spread of learning, is the heartfelt

wish of every member of that body on whose behalf we now address you.

T. E. Thorpe, *President.*
William A. Tilden, *Treasurer.*
Wyndham R. Dunstan, Alexander Scott, } *Secretaries.*
Raphael Meldola, *Foreign Secretary.*

Of the following papers those marked * were read:—

*76. "*The Hydrosulphides, Sulphides, and Polysulphides of Potassium and Sodium.*" By W. Popplewell Bloxam.

In this paper the author shows that there is a very important difference between treating the aqueous solution of a sulphide and one of a hydrosulphide with sulphur. When sulphur is added to aqueous solutions of potassium and sodium sulphides, some thiosulphate is always formed along with the polysulphide, whilst hydrogen sulphide is evolved. This points to the sulphide having become, in part at least, hydrolysed into hydroxide and hydrosulphide. The action of sulphur on aqueous solutions of the pure hydrosulphides gives pure polysulphides with evolution of hydrogen sulphide.

The various wet and dry methods of preparing the sulphides and polysulphides of potassium and sodium described by the many authors who have worked at this subject have been repeated by the author, who concludes that (1) none of these authors could have obtained any polysulphide pure, but only a mixture of polysulphide and thiosulphate; (2) no method exists for separating the polysulphide from the thiosulphate.

The author has succeeded in obtaining the following hydrates of potassium sulphide: $K_2S,2H_2O$; $K_2S,5H_2O$; $K_2S,12H_2O$. These salts can be dehydrated in a current of dry hydrogen, and the potassium sulphide remains stable at 560°. As $K_2S,5H_2O$ loses $5H_2O$, it is evidently not $KHS,KHO,4H_2O$. Sodium sulphide was obtained as $Na_2S,9H_2O$.

By saturation of a solution of potassium hydroxide with hydrogen sulphide, crystals of the composition $2KHS,H_2O$ were obtained, which, like the hydrates of the normal sulphide, could be dehydrated without loss of sulphur. The hydrosulphide was quite stable at 560°.

According to Sabatier, the hydrated crystals of sodium sulphide are easily converted into sodium hydrosulphide by the action of hydrogen sulphide; but the author shows that solutions of sodium sulphide will only take up sufficient hydrogen sulphide to form the hydrosulphide under certain rather restricted conditions as to concentration and temperature. Under favourable conditions, two hydrates were obtained, $NaHS,2H_2O$, $NaHS,3H_2O$, the latter being the stable form.

To prepare the polysulphides, sulphur was dissolved in gently heated solutions of the hydrosulphides, when the following potassium compounds were obtained:— $K_4S_5,10H_2O$, $K_4S_8,6H_2O$, $K_4S_8,19H_2O$, $K_4S_9\,xH_2O$, K_4S_{10},xH_2O, as well as substances approximating in composition to K_4S_6 and K_4S_7.

The only sodium compound obtained in this way was $Na_4S_9,14H_2O$.

*77. "*On the Relative Efficiency of Various Forms of Still-head for Fractional Distillation.*" By Sydney Young, D.Sc., F.R.S.

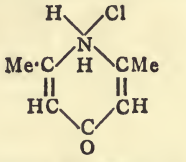
Experiments have been made to test the efficiency of the following forms of still-head, most of which are in general use: (1) plain vertical tubes of different lengths and widths; (2) sloping and spiral tubes; (3) vertical tube with bulbs (Wurtz); (4) the Hempel still-head; (5) the Glinsky dephlegmator; (6) the Le Bel-Henninger dephlegmator. In addition to these a modified Young and Thomas dephlegmator and three new forms of still-head, descriptions of which are given in the paper, have been tested and compared with the others.

As the amount of liquid available for fractionation is often very limited, special attention has been paid to the suitability of the various forms of still-head for the distillation of small as well as of large quantities of liquid. Taking both efficiency and usefulness into account, it is shown that the new forms of still-head are superior to those in general use.

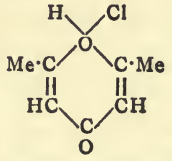
*78. "*The Salts of Dimethylpyrone and the Quadrivalence of Oxygen.*" By J. N. Collie, Ph.D., F.R.S. and Thomas Tickle.

The authors have investigated the series of salts formed by dimethylpyrone with acids. Dimethylpyrone forms, in aqueous solutions with various acids, crystallisable salts. The hydrochloride, hydrobromide, hydriodide, nitrate, oxalate, tartrate, chloracetate, salicylate, picrate, and platinochloride, were prepared; these compounds are produced by direct addition of the acid to the dimethylpyrone without the elimination of water, as in the equation $C_7H_8O_2+HCl=C_7H_8O_2HCl$. On solution in much water, they again break up into dimethylpyrone and the free acid.

Taking into account the molecular structure of dimethylpyrone, the method of preparation, and the properties of these compounds, the authors are inclined to believe that their constitution is similar to that of the salts of nitrogenous and other bases.



Dimethylpyridone chloride.



Dimethylpyrone chloride.

This, however, assumes that oxygen may behave as a quadrivalent element. In favour of this hypothesis, the authors instance such compounds as dimethyl ether hydrochloride, diethyl ether hydriodide, ether peroxide, &c., and they suggest that should compounds similar to the salts they have examined contain nitrogen, phosphorus, sulphur, or iodine, they could be regarded as derived from the hypothetical bases, NH_4OH, PH_4OH, SH_3OH, IH_2OH respectively; hence dimethylpyrone may be looked upon as a derivative of OH_3OH or *oxonium hydrate.*

79. "*The Symmetrical Di-isopropylsuccinic Acids.*" By William A. Bone and C. H. G. Sprankling.

The authors have succeeded in preparing two isomeric symmetrical di-isopropylsuccinic acids, by the action of isopropyl bromide on the sodium derivative of ethyl isopropylcyansuccinate, and subsequent hydrolysis of the ethereal salt so obtained.

The *trans*-acid, which is quite insoluble in benzene, melts at 226° and has a dissociation constant $k=0{\cdot}0108$. The *cis*-acid, which dissolves in warm benzene, melts at 171—172°, and has a dissociation constant $k=0{\cdot}2255$. Both acids, on treatment with acetyl chloride, give their anhydrides, which are liquid. The anhydrides dissolve in sodium hydrate, forming the sodium salts of the original acids. The anhydride of the *trans*-acid, on being boiled with acetic anhydride for several hours, is converted into the *cis*-anhydride, so that, in this way, the *cis*-acid can be obtained from the *trans*-modification. The behaviour of the new acids with acetyl chloride and acetic anhydride is thus in all respects similar to that of the symmetrical dimethylsuccinic acids. The calcium salts of both acids are sparingly soluble.

Previous workers (Hell and Mayer, *Ber.*, 1889, xxii., 48; Auwers, *Ann.*, 1896, ccxcii., 162) have been able to obtain only the *cis*-acid. Auwers (*loc. cit.*) states that symmetrical di-isopropylsuccinic acid, unlike other symmetrical di-alkylsuccinic acids, exists only in one modification. The authors are also completing an investigation on the symmetrical dipropylsuccinic acids.

80. "*Active and Inactive Phenylalkyloxyacetic Acids.*" By ALEX. MCKENZIE, M.A., D Sc.

The replacement of the alcoholic hydrogen in active malic, lactic and tartaric acids by alkyl groups causes a striking increase of optical activity. The primary object of the investigation was to ascertain the effect of a similar replacement in the much more highly active mandelic acid.

For the preparation of the active alkylated mandelic acids, the method of alkylation recently applied by Purdie and Pitkeathly (*Trans.*, 1899, lxxv., 157) was adopted. Preliminary experiments with inactive mandelic esters showed that phenylalkyloxyacetic esters were produced. It was found convenient to start with free mandelic acid instead of its esters; thus, by the action of silver oxide and alkyl iodide on *i*-mandelic acid, phenylalkyloxyacetic acids were obtained.

By the interaction of silver oxide, ethyl iodide, and *l*-mandelic acid, a mixture of ethyl *l*-mandelate and *l*-phenylethoxyacetate results. After hydrolysis, *l*-phenylethoyxacetic acid was completely separated from mandelic acid as an oil. Polarimetric observations were made on the acid and on its sodium and barium salts.

l-Phenylmethoxyacetic acid is crystalline, m.p. 63—64°. The sparing solubility of its sodium salt in water afforded a ready method of separating it from mandelic acid. Rotations of the acid in various solvents and of several of its salts in water were made.

From *l*-mandelic acid, phenylpropyloxyacetic acid was obtained as an inactive oil; phenylisopropyloxyacetic acid was crystalline and active.

The molecular rotations of *l*-phenylmethoxyacetic acid and its salts are slightly higher than those of *l*-mandelic acid for equivalent concentrations. The rotations fall on dilution, a minimum being reached with the easily-dissociated salts, but with the acid—which in about 1/50 normal solution is 18 per cent dissociated—the minimum had not been reached. Rimbach's results with *d*-mandelic acid (*Zeit. Physikal. Chem.*, 1899, xxviii., 251) show similar relationships. The rotations for the ethoxy- and isopropyloxy-acids are considerably lower than those of *l*-mandelic acid.

Silver oxide has been used as an alkylating agent with tartrates and lactates without any observations of racemisation in the active products. Although every precaution was taken to avoid racemisation, so far, at least, as this is caused by violent action and rise of temperature, the propyloxy-acid was obtained inactive. Partial racemisation had also taken place in the preparation of ethyl *l*-phenylethoxyacetate by the silver salt method.

81. "*The Chemical Composition of the Oleo-resin of Dacryodes Hexandra.*" By A. MORE.

The oleo-resin consists of essential oil, a resin, and a white crystalline substance, $C_{25}H_{44}O$, melting at 166—167°.

The essential oil contains *lævorotatory pinene* and *lævorotatory sylvestrene*, which is the optical isomer of the sylvestrene described by Atterberg.

The crystalline substance is insoluble in water, and only sparingly soluble in strong alcohol. By the action of acetic anhydride it yields a crystalline mono-acetate, m.p. 200°, and it therefore appears to be an alcohol. It is unaffected by potash and by all ordinary reagents. A tetranitro-derivative is produced by the action of fuming nitric acid. Chromic acid in acetic acid solution, while oxidising it, appears to cause two molecules to combine; the product is a feeble acid, the molecular weight of which was determined by the cryoscopic method. The substance is probably identical with Personne's ilicic alcohol, m. p. 175°, with which it agrees in composition, and which gives an acetyl derivative melting at 204—206°.

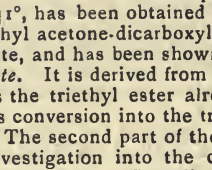
82. "*The Condensation of Ethyl Acetonedicarboxylate: the Constitution of Triethyl Orcintricarboxylate.*" By DAVID SMILES JERDAN.

In the first part of this paper the author discusses the action of condensing agents on ethyl acetonedicarboxylate. Two condensation agents have already been described, namely, a triethyl orcintricarboxylate, $C_{16}H_{20}O_8$ (Cornelius and von Pechmann, *Ber.*, 1886, xix., 1446; von Pechmann and Wolman, *Ber.*, 1898, xxxi., 2014), and a lactone, $C_{12}H_{10}O_7$, which was discovered by the author (*Trans.* 1887, lxxi., 1106), and shown to be a derivative of phloroglucinol. Triethyl orcintricarboxylate was originally obtained by the action of sodium on ethyl acetone dicarboxylate, and afterwards by dissolving the ester in alcohol, saturating the solution with hydrogen chloride, and allowing the mixture to stand some weeks. The lactone, $C_{12}H_{10}O_7$, was first prepared by the action of sodium on ethyl acetone dicarboxylate dissolved in benzene. The author has recently found that both substances are formed by the action of sodium ethylate on an alcoholic solution of ethyl acetone dicarboxylate, and further, that small quantities of a number of metals and of their oxides are capable of bringing about the condensation of relatively large quantities of ethyl acetonedicarboxylate. Thus the ester, when heated with 1/800th part of its weight of sodium, gives a 30 per cent yield of triethyl orcintricarboxylate. The probable course of this reaction is discussed.

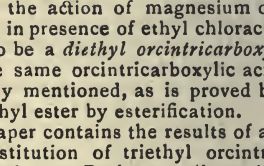
A new condensation product, $C_{14}H_{16}O_8$, which melts at 141°, has been obtained by the action of magnesium on ethyl acetone-dicarboxylate in presence of ethyl chloracetate, and has been shown to be a *diethyl orcintricarboxylate*. It is derived from the same orcintricarboxylic acid as the triethyl ester already mentioned, as is proved by its conversion into the triethyl ester by esterification.

The second part of the paper contains the results of an investigation into the constitution of triethyl orcintricarboxylate. Cornelius and von Pechmann (*loc. cit.*) pointed out that this substance may have one or other of the two formulæ:—

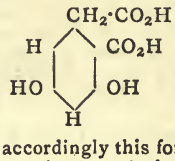
I.

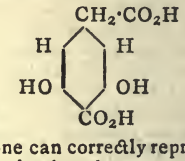


II.



The author has obtained from triethyl orcintricarboxylate, and from the diethyl orcintricarboxylate (m. p. 141°) already mentioned, derivatives of two orcindicarboxylic acids, both of which have been shown to contain the group $-CH_2-COOH$. Only formula I., the asymmetric formula for triethyl orcintricarboxylate, admits of the formation of two such acids, namely:—





and accordingly this formula alone can correctly represent the constitution of triethyl orcintricarboxylate.

83. "*A Series of Substituted Nitrogen Chlorides.*" By F. D. CHATTAWAY and K. J. P. ORTON.

Compounds in which halogen is attached to nitrogen have been little studied, although a number of isolated examples are known. In continuation of our work on nitrogen iodide, we have studied this nitrogen halogen linkage, and have obtained a very large number of compounds in which it occurs.

In this paper the disubstitution products of nitrogen chloride are considered, containing formyl, acetyl, and benzoyl, together with a phenyl or a substituted phenyl residue.

These form a well-defined group of compounds, phenyl acetyl nitrogen chloride discovered by Bender being one of the simplest members,

They are readily obtained from the corresponding formanilide, acetanilide, or benzanilide by the action of hypochlorous acid under regulated conditions.

$$\frac{RCO}{R'}>NH+HOCl=\frac{RCO}{R'}>NCl+H_2O.$$

The method generally employed is to add gradually the calculated quantity of calcium hypochlorite to the anilide suspended in a saturated solution of potassium bicarbonate.

The substituted nitrogen chlorides are all stable solids of low melting point, crystallising well in large, colourless, transparent plates or prisms. They dissolve readily in chloroform, carbon bisulphide, and benzene, but only sparingly in ligroin.

They react very readily with hydrochloric acid, hydriodic acid, and alkaline hydrogen peroxide, liberating chlorine, iodine, and oxygen respectively, and reforming the anilide. They act with great energy upon aniline, giving chloranilines. The most remarkable change, however, which these compounds undergo takes place when they are heated. When an unsubstituted phenyl group is attached to the nitrogen, the chlorine and the para-hydrogen atom of the nucleus change places, and a para-chloranilide is formed. With a para chlorphenyl group attached to the nitrogen, a similar change takes place on heating, the chlorine, however, now going into the ortho-position. Similar changes are brought about when these nitrogen chlorides are warmed with water or dilute acids.

If, however, both the para- and ortho-positions in the phenyl nucleus are occupied, *e.g.*, by chlorine atoms, no intramolecular change ensues, but the molecule breaks down in a somewhat complicated way which apparently depends on the nature of the acid radicle attached to the nitrogen; in the case of the formyl and acetyl derivatives, chlorine is set free; with the benzoyl compound, benzoyl chloride is evolved. Phenyl acetyl nitrogen chloride has been prepared by the bicarbonate method, a theoretical yield being obtained; it crystallises in large, transparent plates.

The following compounds have been prepared:—

Phenylformyl nitrogen chloride, $HCON(C_6H_5)\cdot Cl$, long, transparent prisms. M. p. 47°. *Para-chlor-phenyl formyl nitrogen chloride*, $HCON(C_6H_4Cl)\cdot Cl$, long, transparent prisms. M. p. 95—96°. 2 : 4-*dichlor-phenyl formyl nitrogen chloride*, $HCON(C_6H_3Cl_2)\cdot Cl$, colourless, transparent plates. M. p. 44°. *Para-chlor-phenyl acetyl nitrogen chloride*, $CH_3CON(C_6H_4Cl)\cdot Cl$, colourless plates. M. p. 82°. 2 : 4-*dichlor-phenyl acetyl nitrogen chloride*, $CH_3CON(C_6H_3Cl_2)\cdot Cl$, large, glittering plates. M. p. 68°. *Phenyl benzoyl nitrogen chloride*, $C_6H_5CON(C_6H_5)\cdot Cl$, colourless plates. M. p. 77°. 2 : 4-*dichlor-benzoyl nitrogen chloride*, $C_6H_5CON(C_6H_3Cl_2)\cdot Cl$, large, colourless plates. M. p. 86°.

We believe that the oil obtained by Witt, and regarded by him as a hypochlorous acid addition product of 2 : 4-dichlor-acetanilide, is impure 2 : 4-dichlor-phenyl acetyl nitrogen chloride.

PHYSICAL SOCIETY.

Ordinary Meeting, June 9th, 1899.

Prof. OLIVER LODGE, F.R.S., President, in the Chair.

THE SECRETARY read a paper by Mr. C. G. LAMB "*On the Distribution of Magnetic Induction in a Long Iron Bar.*"

A Lowmoor iron rod, whose length was 250 times its diameter, was taken, and a B-H curve plotted by ballistic measurements made with a search coil at the centre of the bar. The search coil was then moved along the bar, and the distribution of induction was determined for magnetising forces varying from H = 0·74 to H = 35·0. Up to fields of 3·35 the induction leaks out more and more quickly as H increases, but above this value the induction tends to keep in more and more. From the curves obtained the mean induction was deduced, as well as the distance of the resultant pole from the middle of the bar. It is shown that this distance first decreases and then increases with the rise in field strength. According to the ellipsoidal theory it should be constant. The bar was then made into a ring, and the B-H curves again determined. From these curves—together with known relations between B, H, and p—curves showing the variation of p along the bar were constructed.

The CHAIRMAN gave a general explanation of the way the leakage depended upon the permeability in the case of a long iron bar.

A paper "*On the Absolute Value of the Freezing-point*" was read by Mr. ROSE INNES.

The corrected values of the absolute value of the freezing-point, determined by Lord Kelvin from experiments on hydrogen, air, and carbonic acid, contain discrepancies amounting to $\frac{1}{3}$ per cent between the carbonic acid and the hydrogen, while the separate measurements for carbonic acid agree among themselves to about $\frac{1}{6}$ per cent. Starting with Lord Kelvin's equation for the forcing of a gas through a plug, the author has obtained a formula for the absolute value of the freezing-point, which can be worked out from the experimental researches of Regnault. The formula is based on the experimental proof by Joule and Kelvin, that the ratio between the cooling effect for atmosphere of differential pressure and the pressure is constant for all pressures. Applying data from Regnault's experiments to the formula deduced by the author, the values of the freezing point are practically the same as those given by Lord Kelvin. Hence it is thought probable that the discrepancies are due to inaccuracies in the experiments of Regnault which were conducted at constant pressure. The value of the zero calculated from experiments on hydrogen at constant volume made by M. Chappuis, is, if we treat hydrogen as a perfect gas, 237·034. Applying a thermodynamic correction for the deviation of hydrogen from the laws of a perfect gas, the value of the freezing-point becomes 273·19. This figure agrees very closely with the value 273·14 obtained by Lord Kelvin from the constant pressure experiments on air. The correction has only been applied to hydrogen, because in this case it is so small that a large percentage error in its determination has a very small effect upon the absolute value of the freezing-point. In constant-pressure work the experiments are difficult to carry out, and the correction is easily applied while in constant-volume work, the experiments are easily performed, and the thermodynamic correction is difficult to apply.

Prof. GRAY expressed his interest in the manner in which Mr. Rose-Innes had obtained his results without using the experimental data of Joule and Kelvin, and pointed out that Lord Kelvin attached most importance to the results he had obtained for air. It would be useful to have the gas constants re-determined with greater accuracy. The compensating arrangement devised by Prof. Callendar would enable experiments at constant pressure to be carried out satisfactorily.

Dr. LEHFELDT drew attention to the sign of the correction applied by the author, and asked if it should not be negative instead of positive. He pointed out that variation in the specific heat of a gas might affect the formula, and said that Boltzmann had shown that it was impossible to determine an absolute temperature without introducing calorimetric measurements. As Joule and Kelvin had sometimes found positive and sometimes negative values for the cooling effect in the case of hydrogen large percentage errors might occur in the value of the correction.

Mr. BLAKESLEY asked what the probable error was in the numbers given by Lord Kelvin.

Mr. WATSON said that the author had calculated the

value of the freezing-point from experiments on hydrogen, and had shown that the result agreed closely with the value of the zero deduced by Lord Kelvin from experiments on air. He would like to know what agreement would be got by applying Mr. Rose-Innes's correction to the case of air.

Mr. Rose-Innes, in replying, said he agreed with Prof. Gray that it would be useful to have the contents redetermined. It was only in their early work that Joule and Kelvin observed a cooling effect for hydrogen, the bulk of the experiments giving a heating effect. The sign of the correction depended on the increase or decrease of the effect with temperature, and was positive in the case of hydrogen. Regnault has proved experimentally that the value of the specific heat is constant.

NOTICES OF BOOKS.

A History of Physics in its Elementary Branches, including the Evolution of Physical Laboratories. By Florian Cajori. New York and London: Macmillan and Co. 1899. Pp. viii.—322. 8vo. Ill.

Works on the history of the comprehensive subject of physics are not numerous; that by Joh. Christ. Sturmuis, published at Nuremberg in 1676, recorded the notable inventions made in the earlier part of the seventeenth century, and is of antiquarian interest merely. Germany has produced several:—J. C. Fischer's "Geschichte der Physik (1801-1808), extends to eight volumes; August Heller's work with the same title (1882-84), in two volumes; Poggendorff's "Geschichte" (1879), in one volume, and Rosenberger's treatise embodying synchronistic tables (1882-90), in three volumes, are the principal ones in the German language. In the French language we have G. Libri's "Histoire" (1838-41), which, however, is confined to Italy; A. Libe's "Histoire Philosophique" (1810), Max Marie's voluminous work (1883 88), in twelve volumes, and F. Hoefer's condensed sketch in one volume (1872). Authors writing in English seem to have neglected this topic, for if we except Baden Powell's "History of Natural Philosophy" (1842), which moreover omits heat and electricity, and William Whewell's comprehensive "History of the Inductive Sciences" (1837), students will not readily find an English work that covers the field from the earliest period to the present time. This need has now been filled by Dr. Florian Cajori, Professor of Physics in Colorado College. The progress of discovery in mechanics, light, heat, electricity and magnetism, and in sound, is set forth in eight distinct periods, viz., the Greeks, the Romans, the Arabs, the Middle Ages, the Renaissance, the Seventeenth Century, the Eighteenth Century, and the Nineteenth Century. There are also chapters on the Causes of Failure of Greek Physical Inquiry, and on the Inductive Method of Scientific Inquiry, which latter is rather brief and inadequate; numerous references, however, in the footnote enable a student to extend his reading on the subject. These references to authorities are very numerous throughout the work, and form a valuable feature, furnishing proofs of statements as well as means of pursuing the topics in greater detail. The author shows a wide knowledge of the sources of history, not merely of the standard works, but the isolated essays and notes scattered throughout periodicals. This has enabled Professor Cajori to give credit wherever it is due, without national bias.

In the preface the author refers to the necessity of limiting the size of the book and the consequent omission of a few subjects that properly belong to elementary physics; this restriction to 300 pages has caused utmost condensation and prevented the author from elaborating the vast number of topics, giving the work a paragraphic style that does him injustice. We hope that the work may soon go to a second edition, and that author and publisher may see fit to enlarge the volume 50 per cent.

Biographical sketches of those who have contributed to the advancement of physical science occur throughout the book, which is brought down to the current decade.

A concluding chapter deals with the evolution of physical laboratories. The illustrations are few in number and portraits are notably lacking. The index is full. The reviewer knows of no book in the English language that covers the ground so satisfactorily as the one before him.

H. C. B.

Handbook of Public Health, Laboratory Work, and Food Inspection. Part I. By O. W. Andrews, M.B., B.S., M.R.C.S., Surgeon R.N., &c. Portsmouth: Charpentier and Co. Pp. 66.

The volume now before us is the first of three, comprising a series of Lectures delivered by the author to the Surgeons on Entry, Royal Navy.

Vol I. treats of the points to be observed in the inspection of fish, flesh, and fowl, intended for human food, so far as they are dealt with in the course of instruction at the R. N. Hospital, Haslar.

A number of illustrations are given of parasites, &c., injurious to human beings, as well as various fish found in distant parts of the world; a good rule to remember with regard to fish is, that those with scales are wholesome, while those without are not.

Chemical Analysis, Qualitative and Quantitative. By W. Briggs, M.A., LL.B., F.C.S., and R. W. Stewart, D.Sc. (Lond.). The University Tutorial Series. London: W. B. Clive. Pp. 128.

This is a useful book for beginners, and appears to be specially adapted for those students who are unable to attend regular laboratory classes, but have to depend to a great extent on their own resources at home. Instead of only the bare instructions being given for carrying out analytical operations, the reason for each step is explained, and also the action or reaction that takes place; for this reason the book is slightly larger than most books for beginners, a fact which is, however, justified by the result.

Chemical Novelties for 1899. ("Les Nouveautés Chimique pour 1899"). By C. Poulenc. With 196 Figures in the Text. Paris: Baillière et Fils. 1899. Pp. 364.

The latest forms of apparatus used in chemical laboratories are reviewed in this volume. As the science of chemistry advances, so must the apparatus be modified and improved. The brilliant work of M. Moissan, in Paris, and Prof. Dewar, Lord Rayleigh, and Prof. Ramsay, in our own country, necessitate constant improvement and invention in the tools and material of the chemist. In the first chapter descriptions will be found of physical apparatus used particularly in chemistry, among which are G. Müller's compensation thermometer, Schlœsing's apparatus for determining the density of small volumes of gas, picnometers by Fuchs, Landsberg's method for the determination of molecular weights by boiling-points, &c.

In Chapter II. improvements in furnaces, ovens, refrigerators, &c., are described, as well as a new method for the manufacture of acetylene, new mercury pumps, air compressors, &c.

The third Chapter deals with general analysis, special mention being made of Leger's eudiometer and Buisson's apparatus for gas analysis; in metallurgical analysis we find Campredon's method for the estimation of sulphur, and a new microscope by Retjo for the examination of metals.

Chapter IV. deals with electricity, and Chapter V., and last, describes all the latest forms of apparatus employed in the important and growing science of bacteriology.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 20, May 15, 1899.

A New Preparation and some New Properties of Pentabromide of Tungsten. — Ed. Defacoz. — The action of dry gaseous hydrobromic acid on pure hexachloride of tungsten affords a new method of preparation of tungsten pentabromide. The action takes place at about 250°. The pentabromide thus obtained is well crystalline in needles. It is very hygroscopic and easily decomposes in presence of water, giving the blue oxide. It is soluble in a great number of liquids—carbon tetrachloride, chloroform, bromoform, absolute alcohol, ether, terebene, and benzene—but the solvent must be completely anhydrous. That it has been obtained in a good state of purity is proved by analysis.

Mixed Halogen Salts of Lead.—V. Thomas.—In a recent paper the author showed that chloride and iodide of lead were susceptible of uniting in equal molecular weights to form a well-defined chloriodide. The present paper gives an account of the further study of this and other mixed lead halogen salts. Chlorobromides are formed by the following methods:—(1) Action of hydracids on the halogen salts of lead. (2) Solution of lead chloride in a solution of bromide or *vice versa*. (3) Action of chloride and bromide of an alkali on chloride and bromide of lead. (4) Action of bromine on chloriodides. The last two methods give the best results. The compound formed is anhydrous and crystalline, and can be kept for some months without decomposition; it is soluble in water, but is liable to be decomposed if the solution is very dilute. Bromiodides are produced under analogous conditions to those which produce the chlorobromides.

Separation and Estimation of Traces of Bromine in presence of a large Excess of Chlorine.— H. Baubigny.—In a very recent paper, the author described a method by which minute traces of bromine could be estimated in a large excess of chloride solution, by treating a concentrated solution of the chloride with a mixture of permanganate and copper sulphate. The present paper describes an improved method. Instead of employing the oxidising mixture, a small amount of chlorine is added to the chloride solution—sufficient to displace the bromine. By this method the whole analysis can be completed in four or five hours, and with very great accuracy. It has been possible to recognise and to estimate less than half a milligrm. of bromine in 10 grms. of sea-salt.

Activity of Manganese in Relation to the Phosphorescence of Sulphide of Strontium. — José Rodriguez Mourelo.—M. Lecoq de Boisbaudran has made experiments *in vacuo* on the phosphorescence of mixtures of different substances containing small quantities of sulphate of manganese which in themselves were not phosphorescent when subjected to electric action. The author continues this research by investigating the phosphorescent properties of manganese when mixed with sulphide of strontium without using a vacuum or electric current, and he finds that, in the same manner as the sub-nitrate of bismuth, carbonate of manganese dissolved in a quantity of sulphide of strontium, renders the latter phosphorescent, with a very clear dark green light, after the mixture has been heated to redness for about three hours—the necessary time for the luminous property to develope with the greatest intensity.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., September 26, 1898.

Partial Racemisation.—A. Ladenburg and G. Doctor.—The authors have attempted to prepare a semi-racemic salt; they tried the neutral racemate of strychnine, which crystallises in warm water in needles fusible at 222°. To prove that this salt is not a mixture, but a well-defined chemical compound, they compared it with the right- and left-handed tartrates, and found that its properties were not those of a mixture; especially, its density is not the mean of the two others, and a mixture of equal parts of the right- and left-handed salts melts at 234°.

Adipic Aldehyde.—A. Baeyer.—Fifty grms. of suberic acid are treated with 100 grms. of tribromide of phosphorus and 180 grms. of bromine for eight to ten hours on a water-bath, the dibromo-suberic acid formed is precipitated with cold water and re-crystallised in boiling water. 30 grms. of this acid are then heated with 60 grms. of crystallised baryta and 90 grms. of water, with a reflux condenser fitted to the flask. The barium salt of dioxysuberic acid which is deposited is decomposed by sulphuric acid, and the dioxysuberic acid is crystallised in boiling water. To effect oxidation, dioxysuberic acid (10 grms.), binoxide of lead (20 grms.), acetic acid (30 grms.), and phosphoric acid at 25 per cent (30 grms.) are heated on the water-bath for four hours. The product is then drawn off by a current of steam. Under these conditions, the adipic acid which is at first formed is immediately transformed either into polymers or into the *cyclopentenemethylal*-1. This aldehyde occurs in the form of a mobile liquid having an odour similar to that of benzaldehyde; it decomposes very rapidly and is easily soluble in water.

Combinations of Chloral with Formic Aldehyde.—A. Pinner.— Formic aldehyde unites very easily with chloral in the presence of concentrated sulphuric acid, giving rise to a sort of oily molecular compound, insoluble in water, completely dissociated on distillation, and partially decomposed by water at the ordinary temperature. If, however, we use a large excess of sulphuric acid, we obtain two crystalline products having the formulæ $(C_3H_3Cl_3O_2)_2$ and $C_5H_4Cl_6O_3$, and a third resinous body. These three bodies behave in the same way as the products of condensation of chloral and the aromatic carbides described by v. Baeyer. The resinous compound has the formula $C_5H_6Cl_6O_4$; boiling alcoholic potash splits it up into oxalic and glycolic acids.

Tautomery of Acetylacetic Ether.—K. Schaum.—A controversial paper, not suitable for abstraction.

On δ-Dimethyl-levulic Acid (Methyl-2-hexanone-3-oïc).—D. Tiemann and F. W. Semmler.—The authors have identified the ω-dimethyl-levulic acid which they obtained by the oxidation of tanacetophorone with the δ-dimethyl-levulic acid described by MM. Fittig and Conrad; it melts at 42—43°. Its oxime,—

$$CH_3.CH.C(NOH).CH_2.CH_2.CO_2H$$
$$\quad\quad\quad

formed into a lead salt, and this latter decomposed by sulphuretted hydrogen. This acid is in the form of a crystalline mass soluble in ether, fusing with decomposition at 186—188°. Aqueous solutions of this acid lose carbonic acid on boiling. To prepare the isomeric dicarbonic acids, the tetracarbonic acid is heated at 160° to tranquil fusion, the residue (40 grms.) is dissolved in warm acetic anhydride (150 grms.), and the product submitted to fractional distillation in vacuo. The portion passing at 215—225° at 90 m.m. is the anhydride of the cis-pentamethylenedicarbonic acid, $C_5H_8(CO)_2O$. The cis acid is partially transformed into the cis-trans by heating it with water or hydrochloric acid in a sealed tube to 180°. The alkaline salts of these two acids are hygroscopic masses extremely soluble in alcohol and water.

Action of Chlorofumaric Ethers on the Amidoximes.—C. Wolf.—When we heat a solution of benzylamidoxime in absolute alcohol with chlorofumaric acid in the presence of ethylate of sodium on a water-bath, we obtain among the products of the reaction a compound possessing acid properties and answering to the formula $C_{13}H_{12}N_2O_4$; it crystallises in long silky needles fusible at 154°; it is not coloured by ferric chloride, and does not fix bromine; its argentic derivative, $C_{13}H_{11}N_2O_4Ag$, melts at 94°. The methylic ether crystallises in flakes fusible at 104° and soluble in dilute alcohol. The corresponding acid is barely soluble in the organic solvents. Phenylethylenamidoxime and chlorofumaric ether unite, giving a compound fusing at 158°.

On Azelaone and Azelaol.—K. Derlon.—The author has studied the products of the dry distillation of azelaate of calcium, looking specially for the octomethylenecetone which should be formed according to the equation—

$$CH_2\begin{matrix}CH_2.CH_2.CH_2.CO_2\\CH_2.CH_2.CH_2.CO_2\end{matrix}>Ca =$$
$$= CaCO_3 + CH_2\begin{matrix}CH_2.CH_2.CH_2\\CH_2.CH_2.CH_2\end{matrix}>CO.$$

An oily layer was first obtained on heating small portions of the salt with its own weight of slaked lime. This product is purified first by a current of steam, then by fractional distillation in vacuo; finally, three portions are isolated, boiling respectively at 45—80°, 80—91°, and 91—105° at 22 m.m. The second fraction answers to the formula $C_8H_{14}O$; it gives a bisulphitic derivative, crystallised in extremely deliquescent small flakes, which could not be purified. The reduction of octomethylenecetone by means of sodium and boiling alcohol gives rise to the formation of the corresponding alcohol, azelaol, a liquid slightly soluble in water, boiling at 187—188° at 746 m.m.

On Methylasparagine.—A. Piutti.—Methylasparagine was obtained by the action of ammonia on citraconic anhydride,—

$$\begin{matrix}CH.CO\\\|\\CH_3.C—CO\end{matrix}>O + 2NH_3 = \begin{matrix}CH_2—CO.NH_2\\|\\CH_3.C(NH_2).CO_2H\end{matrix}.$$

The operation is effected in an autoclave heated to 108—110°. 30 c.c. of the anhydride and 250 c.c. of saturated alcoholic ammonia are used. After six hours the product is evaporated to drive off the ammonia and alcohol, and the methylasparagine is transformed into its cupric derivative in blue clinorhombic plates, soluble in water, having the formula $(C_5H_9N_2O_3)_2Cu.2H_2O$. This salt is then decomposed by a current of sulphuretted hydrogen, and methylasparagine (glutamine) is obtained in the form of efflorescent rhombic tables containing 1 molecule of water; it melts at 254—256°, and is slightly soluble in alcohol; it does not precipitate the salts of silver, lead, or calcium; the salts it forms are very soluble.

Preparation of Phenylhydrazone of Alloxane from Barbituric Acid.—O. Kuhling.—A solution of chloride of diazobenzene is poured gradually into an aqueous solution of barbituric acid and hydrochloric acid. A yellow crystalline precipitate is formed, fusible at 284°, almost insoluble in water, alcohol, and ether.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th instant, His Grace the Duke of Northumberland, K.G., President, presiding. The following were elected members:—Mrs. C. M. Armstrong, Mr. R. Bentley, Sir E. Courtenay Boyle, K.C.B., Mr. R. M. Cowie, Mr. H. H. Cunynghame, Mrs. H. H. Cunynghame, Mr. H. W. Grigg, Mr. O. V. Kilvington, Mr. T. Matthews, Mrs. T. L. Mears, Mr. W. B. Myers-Beswick, Mr. T. C. Owen, Mrs. R. Palmer Thomas, Mrs. Twopeny, Mr. T. Terrell, and the Rev. C. E. Wright. The special thanks of the Members were returned to Mrs. Wigan for her donation of £10 10s., and to Mr. Thomas A. Rogers for his donation of £10 10s. to the fund for the Promotion of Experimental Research at Low Temperatures. The special thanks of the Members were returned to Mr. Hugh Spottiswoode for his valuable gift to the Royal Institution of his father's collection of physical apparatus.

Royal Academy of Science of Turin.—In accordance with the will of the late M. le Sénateur Thomas Vallauri, the Royal Academy of Science of Turin will award a prize to whichever scientific man—either an Italian or of any other nationality—who shall, between January 1, 1899, and December 31, 1902, publish the most important research in the domain of physical science in the widest acceptance of the term. Another prize will also be awarded by the Academy — without distinction of nationality—to the *savant* who, between January 1, 1903, and December 31, 1906, publishes the best critical work on Latin literature. The value of each prize will be 30,000 Italian livres net, less the Italian tax, or about £1000. The prizes will be given one year after being awarded. Members of the Academy, either resident or foreign, will not be eligible to compete. No notice will be taken of manuscript work.

MEETINGS FOR THE WEEK.

WEDNESDAY, 21st.—Microscopical, 8. "Notes on some Sponges belonging to the Clionidæ obtained at Madeira," by J. Yate Johnson. Exhibition of Wild Flowers with Microscope, by C. Beck.

HANDBOOK OF PATENT LAW.
By W. P. THOMPSON, C.E., F.C.S., &c.
TENTH EDITION, 1896. ADDENDUM, 1898.
The above well known work has just been thoroughly revised, and the large number of alterations made since 1896 in Continental and Foreign Patent Laws have been summarised in an Addendum corrected to December, 1898. Price complete, 2s. 6d.
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THE CHEMICAL NEWS.

VOL. LXXIX., No. 2065.

THE DIFFUSION OF IONS INTO GASES.*

By JOHN S. TOWNSEND, M.A. (Dublin),
Clerk Maxwell Student, Cavendish Laboratory, Cambridge.

IN the paper upon this subject, the principles upon which the theory of interdiffusion of gases depends, are applied to the diffusion of ions produced by Röntgen rays. When a gas has been left to itself, the conductivity gradually disappears. When no electromotive forces are acting, the loss of conductivity is due partly to positive and negative ions coming into contact with each other, and partly to the effect of the surface of the vessel, which discharges those ions which come into contact with it.

In order to illustrate in a simple way the principles which are involved, we take the case of a gas contained in a metal sphere, and consider what happens to the ions after the gas has been removed from the influence of the rays. For present purposes we may neglect the effect of re-combination.

The ions may be considered as constituting a separate gas, the molecules of which may be either bigger or smaller than the molecules of the gas in which they are immersed. When an ion comes into contact with the surface of the sphere it loses its charge, so that the metal may be regarded as a body which completely absorbs the ions. The reduction in the conductivity by the diffusion of the ions to the sides, is exactly analogous to the removal of moisture from a gas by bubbling it through sulphuric acid. The more rapidly the water vapour diffuses through the gas, the greater will be the number of water molecules which come into contact with the acid round the bubble. If the quantity of moisture which is removed be found experimentally, the coefficient of diffusion of water-vapour into the gas can be deduced (John S. Townsend, *Phil. Mag.*, June, 1898). It would be impracticable to use this method to find the coefficient of diffusion of ions into a gas contained in a large vessel, as the loss of conductivity due to re-combination would be large compared with the loss due to the sides.

The method which was employed was to pass a uniform stream of gas through fine metal tubing, and to allow the rays to fall on the gas immediately before entering the tubing. The bore of the tubing can be so adjusted that the number of ions which come into contact with the sides will be large compared with the number which re-combine. It is convenient to use tubing of such a length that the conductivity will be reduced to about one-half its initial value.

In order to obtain the coefficient of diffusion when the reduction in the conductivity has been found experimentally, the following problem presents itself:—

If a small quantity of a gas, A, is mixed with another gas, B, and the mixture passed along a tube, the sides of which completely absorb A, to find what quantity of A emerges from the tube with B.

It will be immediately seen that if the gases diffuse rapidly into each other, a large proportion of the molecules of the gas A will come into contact with the surface of the tube and will there be absorbed. If, on the other hand, the rate of interdiffusion is very small the molecules of A will travel down the tube in straight lines parallel to the axis of the tube, and practically none of them will come into contact with the surface.

The complete solution of the above problem may be obtained from the following equations:—

$$\frac{1}{\kappa} pu = -\frac{dp}{dx} + nXe,$$

$$\frac{1}{\kappa} pv = -\frac{dp}{dy} + nYe,$$

$$\frac{1}{\kappa} pw = -\frac{dp}{dz} + nZe + \frac{1}{\kappa} pW,$$

and the equation of continuity—

$$\frac{d}{dx}(pu) + \frac{d}{dy}(pv) + \frac{d}{dz}(pw) = 0;$$

where n is the number of ions per cubic centimetre; p, their partial pressure; e, the charge on each ion; X, Y, and Z, the electric forces at any point; u, v, and w, the velocities of the ions; W, the velocity of the gas B through the tube; κ, the coefficient of diffusion of the ions into the gas B.

The partial differential coefficient with respect to the time is omitted from the equation of continuity, as we need only consider the steady state.

The term dp/dz may be omitted from the third equation, as it is small compared with the other terms.

$W = \frac{2V}{a^2}(a^2 - r^2)$; where V is the mean velocity of the gas B, defined by the condition $\pi a^2 V t$ = total volume of gas crossing any section in a time t; a the radius of the tube, and r the perpendicular distance of any point from the axis.

The forces X, Y, Z vanish, since the electrification is too small to contribute appreciably to the motion of the ions.

The boundary conditions are—

$p = 0$ when $r = a$,

$p =$ constant when $z = 0$.

The solution of the problem requires a somewhat lengthy analysis, so that we give here only the final result.

The ratio of the number of ions (or molecules of the gas A), coming out of the tube with B to the number which enter is—

$$R = 4[0{\cdot}1952\,\varepsilon^{-\frac{7{\cdot}313\,\kappa z}{2a^2V}} + 0{\cdot}0243\,\varepsilon^{-\frac{44{\cdot}5\,\kappa z}{2a^2V}} + \&c.],$$

where z is the length of the tube.

The other terms of the series are too small to be taken into consideration.

Having determined the reduction in conductivity due to tubes of different lengths, the following values of the coefficients of diffusion of ions into air, oxygen, carbonic acid, and hydrogen were obtained:—

Table of Coefficients of Diffusion of Ions in Dry Gases.

Gas.	κ for + ions.	κ for − ions.	Mean value of κ.	Ratio of the values of κ.
Air	0·0274	0·042	0·0347	1·54
Oxygen	0·025	0·0396	0·0323	1·58
Carbonic acid..	0·023	0·026	0·0245	1·13
Hydrogen . ..	0·123	0·190	0·156	1·54

Table of Coefficients of Diffusion of Ions in Moist Gases.

Gas.	κ for + ions.	κ for − ions.	Mean value of κ.	Ratio of the values of κ.
Air	0·032	0·035	0·0335	1·09
Oxygen	0·0288	0·0358	0·0323	1·24
Carbonic acid..	0·0245	0·0255	0·025	1·04
Hydrogen . ..	0·128	0·142	0·1350	1·11

We would expect from the experiments that the above numbers are correct to 5 per cent.

Considering one of the equations of motion—

$$\frac{1}{\kappa} pu = -\frac{dp}{dx} + nXe,$$

we see that when $dp/dx = 0$, the velocity u due to the

* Abstract of a Paper read before the Royal Society, May 18, 1899.

electric force X is $nX\epsilon\kappa/p$. If the potential gradient is one volt per centimetre, X = 1/300 in electrostatic units, and the corresponding value of u is—

$$u_1 = \frac{\kappa\epsilon}{300} \cdot \frac{n}{p}.$$

Let N be the number of molecules in a cubic centimetre of a gas at pressure P, equal to the atmospheric pressure, and temperature 15° centigrade, the temperature at which u and κ were determined.

The quotient N/P may be substituted for n/p in the above equation, and since the atmospheric pressure P is 10^6 in C.G.S. units, we obtain—

$$N\epsilon = \frac{3 \times 10^6 u_1}{\kappa}.$$

The following values of $N\epsilon$ thus obtained for different gases are—

Air	$N\epsilon_A = 1{\cdot}35 \times 10^{10}$
Oxygen	$N\epsilon_O = 1{\cdot}25 \times 10^{10}$
Carbonic acid	$N\epsilon_C = 1{\cdot}30 \times 10^{10}$
Hydrogen	$N\epsilon_H = 1{\cdot}00 \times 10^{10}$

The values of u were taken from the table of mean velocities given by Professor E. Rutherford (*Phil. Mag.*, November, 1897). The values of κ which were used are the mean values obtained for dry gases.

Experiments on electrolysis show that one electrodynamic unit of electricity in passing through an electrolyte, gives off 1·23 c.c. of hydrogen at temperatures 15° and pressure 10^6 C.G.S. units. The number of atoms in this volume is 2·46 N, so that if E is the charge on an atom of hydrogen in the liquid electrolyte,—

$$2{\cdot}46\ NE = 1 \text{ electrodynamic unit of quantity}$$
$$= 3 \times 10^{10} \text{ electrostatic units.}$$

Hence—

$$NE = 1{\cdot}22 \times 10^{10},$$

the charge E being expressed in electrostatic units.

Since N is a constant, we conclude that the charges on the ions produced by Röntgen rays in air, oxygen, carbonic acid, and hydrogen are all the same and equal to the charge on the hydrogen ion in a liquid electrolyte.

Professor J. J. Thomson (*Phil. Mag.*, December, 1898) has shown that the charge on the ions in hydrogen and oxygen which have been made conductors by Röntgen rays, is 6×10^{-10} electrostatic units, and is the same for both gases.

Taking this value for the charge e, we obtain the number of molecules in a cubic centimetre of a gas—

$$N = 2 \times 10^{19}.$$

From this we deduce the weight of a molecule of hydrogen, ρ/N,—

$$4{\cdot}5 \times 10^{-24} \text{ grms.}$$

Since, as we have shown, the charge on an ion produced by Röntgen rays is equal to the charge on a hydrogen ion in a liquid electrolyte, this latter charge is also 6×10^{-10} electrostatic units.

Although the value of $N\epsilon$ for hydrogen is 25 per cent less than its value for other gases, we are justified in including hydrogen in the above general conclusion, as we would expect the value of u for hydrogen to be too small. Professor Rutherford makes no mention of having corrected for the presence of air in his apparatus, or of having used perfectly dry hydrogen. If we take the mean value of κ for moist hydrogen, we obtain $N\epsilon_H = 1{\cdot}15 \times 10^{10}$.

In order to prove that the charge on the positive ion is equal to the charge on the negative ion, the ratio of the coefficients of diffusion must be shown to be equal to the ratio of the velocities. Professor J. Zeleny (*Phil. Mag.*, July, 1898) has shown that the negative ions travel faster under an electromotive force than the positive ions, the ratios of the velocities being 1·24 for air and oxygen, 1·15 for hydrogen, and 1·0 for carbonic acid.

The experiments on diffusion show that the ratio of the velocities would be larger in dry than in moist gases; but as this point has not yet been examined by Professor Zeleny, we cannot expect a very close agreement between the ratios which he gives for the velocities and the ratios of the coefficients of diffusion.

We are led to conclude that the charges on the positive and negative ions are equal from another point of view. It has been proved that the mean charge is the same as the charge on an ion of hydrogen in a liquid electrolyte. If the charges differed, one of them would be less than the charge on the hydrogen ion, whereas experiments on electrolysis show that all ionic charges are either equal to the charge on the hydrogen ion or an exact multiple of it.

GRAPHITE: ITS FORMATION AND MANUFACTURE.*

By E. G. ACHESON, Member of the Franklin Institute.

Early History and Recognition.

In the year 1779, Karl Wilhelm Scheele, a young apothecary in the town of Koping, Sweden, a remarkable genius as an investigator, and then in the 37th year of his age, discovered that graphite had an individuality quite apart from molybdenum sulphide, with which it had been until then confounded. He discovered that when it was treated with nitric acid, carbon dioxide was produced, whereas molybdenum sulphide when oxidised produced a white earth, and he drew the conclusion that it must be some kind of carbon, likely of the general nature of coal.

Previous to this discovery by Scheele, a group of minerals including graphite and certain ores of lead, molybdenum, antimony, and manganese (lead sulphide, molybdenum sulphide, antimony sulphide, manganese dioxide) were believed to be one and the same substance, or, at least, members of the same family. This opinion was due to their outward resemblance, and the fact that they produced marks on paper. This confusion naturally led to the application of the same name or names to each of the members of the group, and as graphite had not been recognised by any peculiarity distinctively its own, it received the names molybdæna, plumbago, graphite, and black-lead, which were used in an indiscriminate manner for each of the several substances. The name molybdæna was dropped at an early date, probably immediately following the discovery by Scheele, and there is no known reason why plumbago and black-lead should not have followed its lead, for graphite is the only one of the series not misleading and entirely appropriate, meaning as it does "I write," from the Greek word $\gamma\rho\upsilon\phi\omega$.

Graphite does not seem to have received any particular attention from chemists from the time of the discovery by Scheele until the year 1800. During the last quarter of the eighteenth century, the diamond was the subject of much interest, in a chemical sense, and in the hands of the French chemists it was shown to produce carbon dioxide when ignited in air. In 1796 Smithson Tannant showed that equal weights of charcoal and diamond yielded equal weights of carbon dioxide on burning, and they were thereafter associated together as carbon. In 1800 Mackenzie added graphite to the carbon group, by showing that it also, in equal weight, produced the same weight of carbon dioxide (Roscoe). Thus, in the opening year of the present century, graphite was proven to be an elementary substance. Charcoal, diamond, and graphite were then recognised as three distinct allotropic forms of the element carbon.

Distribution.

Graphite, in a more or less pure state, is quite freely distributed over the earth, but only in a few places is it

* From Advance Sheets of the *Journal of the Franklin Institute*, June, 1899.

found under conditions of purity, quantity, ease of mining, refining, and transportation to market that permit of a profitable business being made of it. Statistics for the six years 1890 to 1895, inclusive, give the world's production as 73,751, 57,220, 54,280, 55,810, 46,951 and 53,955 short tons. This is an average yearly production of 56,994 tons —over 156 tons every day of the year—of a material known to the majority of men as black-lead or plumbago, useful only for writing on paper and polishing stoves.

The production during the years mentioned was contributed to by Austria, Ceylon, Germany, Italy, United States, Canada, Japan, India, Russia, Great Britain, and Spain, the proportionate quantities furnished by these countries being in the order given (*Mineral Industry*, 1898). It will be observed that Great Britain is, with but one exception, the smallest producer; indeed 45 tons cover the total amount reported, and this was mined in 1895. For several centuries Great Britain was one of, or the, largest producer; in fact, in the earliest days of the industry, it was probably the only one. The graphite from the Borrowdale mines in Cumberland was famous as the best for making pencils. In the sixteenth and seventeenth centuries these mines were so productive as to yield an annual revenue of £40,000, although they were only worked a few weeks in the year for fear of exhausting them (Roscoe).

Great differences exist in the structure and purity of the graphites furnished from the various mines. Mother Nature was seemingly not content with making carbon appear in three forms, charcoal, diamond, and graphite, but extended her labours on graphite; and, to the further confusion of the metallurgist and the chemist, made it a family of two members, crystalline and amorphous, two distinct allotropic forms of the allotropic substance, graphite. The product of the Ceylon mines is crystalline, of great purity, analysing in some instances over 99 per cent carbon, while that of the Borrowdale mines is amorphous and also very pure.

The chief impurity in graphite is iron; indeed, its constant presence and frequent large quantity led to the belief, in the early days, that graphite was a carbon-iron compound, and it was even sometimes called carburet of iron.

Uses.

It is quite probable that the first use made of graphite was an instrument for writing. The first account we have of its employment for this purpose is contained in the writings of Conrad Gessner on "Fossils," published in 1565. A picture of a pencil is shown, and, referring to it, he says:—"The pencil represented below is made for writing, of a certain kind of lead (which I am told is an artificial substance termed by some, English antimony), sharpened to a point and inserted in a wooden handle" (Roscoe). This pencil was probably made of graphite from the Borrowdale mines, which, we are told, were in operation in the sixteenth century. Its uses for other purposes than pencils are of much more recent date, probably all of them falling within the present century, and nearly all within the last few years.

The present uses of graphite include the manufacture of pencils, crucibles, stove polish, foundry facing, paint, motor and dynamo brushes, anti-friction compounds, electrodes for electro-metallurgical work, conducting surfaces in electro-typing, and covering the surfaces of powder grains. For most of these purposes it is used in the natural impure state, while for others it is necessary to render it quite pure and free from grit. Its purification is accomplished by a method worked out by Brodie, which consists in first grinding, or otherwise reducing the graphite to a state of fine subdivision, washing out the heavier impurities, mixing 14 parts with 1 part of potassium chlorate and 2 parts of concentrated sulphuric acid, heating on a water-bath for some hours, washing thoroughly and afterwards roasting at a red heat. If silica is present a treatment with hydrofluoric acid is added to the process.

The mining and manufacture of graphite into articles for which it has been found useful give employment to thousands of people. The mines of Ceylon alone, when working to their capacity, employ about 24,000 men, women, and children; the work, however, is done entirely by hand, and in a very crude manner (Watts' "Dict. of Chem.," 1890). In the city of Nüremburg, Germany, the home of the famous Faber pencil, are twenty-six factories, employing about 5500 people in the making of pencils ("Encl. Brit.").

Manufacture.

The rapid increase in the use of graphite, and consequent decrease in Nature's stocks, make the problem of manufacturing it to order a subject of much importance.

When we consider the hundreds of thousands of chemical changes men are constantly putting the elementary bodies through, and the very prominent part taken by carbon in these reactions, it would be rather remarkable if at some point, Nature's method for producing graphite was not discovered. That it is not a very difficult act is evident from the fact that it has been accomplished, in a small way, in several instances.

Mr. Muir, in Watts' "Dictionary of Chemistry," edition of 1890, mentions six recognised methods.

(1) By heating charcoal with molten iron, and dissolving out the iron with hydrochloric and nitric acids.

(2) By the slow decomposition of hydrocyanic acid, and boiling the product with nitric acid.

(3) By evaporating the mother-liquors obtained in making soda: these contain cyanogen compounds which are decomposed at a certain concentration of the liquid with formation of ammonia and graphite.

(4) By leading carbon monoxide over ferric oxide at 300° to 400°.

(5) By the decomposition of carbon disulphide at high temperature, in contact with metallic iron.

(6) By leading carbon tetrachloride over molten pig iron.

Whether or not any of these methods could be developed to a state providing a commercial process, I am not prepared to say, but am inclined to think not. They have always been considered accidents or chemical feats of the laboratory, and in some instances their formation was very objectionable.

The Cowles Bros., of Cleveland, O., are reported to have found that graphite sometimes occurred in or about the charge of an electric furnace. This formation is referred to in one of their patents, and a feature of the patent is a provision to get rid of the material, as it was very objectionable on account of its high electric conductivity. Its formation was not reduced to a method, the causes for, or the exact conditions under which it was made, not having been investigated. It was like some of those in the list of Muir, an accident, and a great nuisance.

Still another way of making graphite was described by G. Rose, in 1872. He exposed a cut diamond, bedded in charcoal, to a temperature equal to molten cast iron, whereupon the surface became coated with graphite. It is safe to say this process will never attain commercial success nor popularity.

Finally, in the "Encyclopædia Britannica" (1890) we are told that "by heating to the high temperature afforded by a powerful galvanic battery, both the diamond and amorphous carbon are converted into graphite." This statement I will refer to later on.

In a paper which I had the honour of presenting to the Institute at its stated meeting of June 21, 1893 ("Carborundum: its History, Manufacture, and Uses"), reference was made to the formation of a black material consisting of a mixture of carborundum and free carbon during the operation of the carborundum furnaces. This was again referred to, and at much greater length, by Mr. Francis A. Fitzgerald, chemist to the Carborundum Company, in a lecture delivered before the Institute on December 11th, 1896 ("The Manufacture and Development of Carborundum at Niagara Falls"), after it had been the subject

of much thought and study, and when I had about concluded the formulation of a theory covering the transformation of amorphous into graphitic carbon.

Very early in my experiments on the manufacture of carborundum, I noticed that graphite occasionally formed in the portion of the furnace charge lying next to the cylinder of granular amorphous carbon, which passed through the centre of the furnace, and which became heated to an extremely high temperature, by the passage of a heavy electric current, and around which the charge was placed to receive the heat necessary for the formation of carborundum. Also that when ordinary bituminous coal coke was used to form the core, quite a large amount of it was converted into graphite, whereas, when petroleum coke was used, very little of it was made graphitic.

By a careful study of these formations, it was found that the graphite formed outside of and surrounding the core was produced by the decomposition of the carborundum, which is, chemically, a carbide of silicon, and, by induction from a number of known facts, that that formed within the core was also produced from a similar decomposition of carbides, which were created by the chemical union of the carbon of the core with its contained impurities. The facts from which I have drawn this conclusion are:—

1. Comparatively pure petroleum coke produces practically no graphite.

2. Impure bituminous coal coke produces large quantities.

3. The larger the known percentage of impurities in the bituminous coal coke, the greater the amount produced.

4. That only a part of the carbon of the core is converted into graphite. This not being increased, even by repeated use of the same grains, in successive carborundum furnaces.

The graphite formed by the destruction of carborundum is remarkable in that it retains the form of the crystal of carborundum from which it is derived. It has, however, less than one-third the weight of carborundum, and possesses the characteristic metallic-grey colour of natural graphite; but in size and form it so closely resembles the original crystal as to be, in fact, its skeleton pseudomorph in graphite. The graphite formed in the core is usually not so well defined, or distinct, as in that from carborundum, most of it being disseminated through the body of the individual grains in which it is found, the amount contained in any one grain varying with the percentage of impurity originally present. In some instances the entire mass of the grain is converted into beautiful graphite, this occurring, I think, in cases where the grain is largely composed of slate, and it sometimes happens that one-half of the grain is completely converted, while the remainder is changed but little.

These two seemingly distinct methods of producing graphite from carborundum and from coke, are, in fact, identically the same; the first step in each is the formation of a carbide, the second its destruction. In making carborundum, silica and coke are mixed in the correct proportions to produce a true carbide, when heated in the electric furnace, without an excess of either constituent In making this mixture, account is taken of the impurities contained in the coke, and the silica reduced proportionately. In the case of the core there is a natural mixture that produces a carbide from a portion of the carbon. The carbides formed under both of these conditions decompose when heated to a certain temperature above that at which they were formed.

This method of manufacturing graphite I would define as consisting in heating carbon, in association with one or more oxides, to a temperature sufficiently high to cause a chemical reaction between the constituents, and then continuing the heating until the combined carbon separates in the free state. It is not, however, limited to the use of oxides, as pure metals; their sulphides and other salts may be used, but for various reasons the oxides are to be preferred.

Theory of Formation.

All of the methods of manufacture, thus far known, contain the same underlying fundamental principle. Each of the six methods described by Muir, as well as my own method, contain as a part of the process the expulsion or liberation of the carbon from a chemical association with one or more elements, and this occurs under conditions unfavourable to, or absolutely prohibitive of, its re-association with the same or other elements. It is cast out, free to take unto itself such physical or other properties as, we must assume, properly belong to it in the free state, when formed under normal conditions. It has been shown by Moissan, that, when subjected to great pressure, at the moment of separation from cast-iron, carbon has those distinctive characteristics that cause it to be called diamond; while Scheele showed, in 1778, that the same carbon, separating from the iron without pressure, takes the graphitic form. Amorphous carbon, the third allotropic form, never occurs pure, and is invariably produced from carbon held in chemical association with other elements, under conditions favourable to free chemical action between it and other elements.

The production of graphite by Rose's method—heating a diamond bedded in charcoal to the melting-point of cast-iron—is a beautiful illustration of the return of a body under strain to the form it takes under normal conditions. It will be noted that the diamond was heated to the temperature at which it is known to form, as shown by Moissan's experiments; also that it was fairly well protected from chemical action.

The statement in the "Encyclopædia Britannica" that both diamond and amorphous carbon are converted into graphite, when heated by a powerful electric current, is very commonly held,—indeed, I might say universally,—although Berthelot concluded, from his investigations, that heat alone is without influence on carbon; that is to say, graphite is not changed to amorphous carbon, nor the amorphous to graphite, when heated to whiteness in an atmosphere of hydrogen or chlorine. That diamond will change to graphite, when protected from chemical influences, under the influences of high temperature, is undoubtedly true, and, indeed, is what might be expected from other known facts; but that *pure* amorphous carbon will change to graphite as the simple result of heating, is not proven, and certainly it does not occur at, or below, the temperature necessary for the transformation of the carbon in a carbide to graphite.

From the facts in hand I have deduced the following theory:—

1. Graphite is the form carbon assumes, when freed from chemical associations, under conditions of low pressure and protection from chemical influence.

2. Diamond is the form carbon assumes, when freed from chemical associations, under conditions of high pressure and protection from chemical influence. And, by inference,—

3. Amorphous carbon is the form carbon assumes, when freed from chemical associations, under conditions of low or high pressure and exposure to chemical influence.

This theory does not, however, account for all of the observed facts, and must be supplemented by the hypothesis that catalysis occurs, under certain conditions, during the transformation of amorphous into graphitic carbon. The amount of graphite produced in the core of a carborundum furnace, and also in graphite articles I have made, is much too great to be accounted for by the theory that it is formed by the dissolution of the fixed carbides, formed by the contained impurities and carbon sufficient to satisfy the chemical formula. The most probable and satisfactory explanation is that a catalytic action occurs—a progressive formation and dissolution of carbides. The temperature being much above the point

of volatilisation of silica, and all other possible impurities, a rapid dissipation of the active agents takes place, and is completed, in this case, before the conversion of all of the amorphous carbon can occur.

Commercial Manufacture.

As the result of my investigations and deductions, I think the only commercial way to make graphite is by breaking up a carbide by the action of heat, The carbon should be freed from chemical combination by what might be termed the evaporation of its associated elementary substances. I have secured patents covering this method, and these have been made the basis for the organisation ef an incorporated company, bearing the name "Acheson Graphite Company." The company has now under way the erection of works at Niagara Falls, where the necessary electric current will be obtained from the Niagara Falls Power Company.

Several distinct forms of the product will be produced. One consists of forms or articles, made out of amorphous carbon, with the desired amount of impurity added thereto, which will afterwards be heated in an electric furnace, and converted, more or less, into graphite. I have been carrying on this line of manufacture for a year or more, using the furnaces of the Carborundum Company to produce the graphitisation, the articles having first been made by the arc-light carbon manufacturers. Over 200,000 carbon electrodes, measuring 15 inches in length, with about 1 inch cross-sectional area, were made for use in the Castner alkali process, nearly one-half of them having been shipped to Europe, to be used for this work in England and Germany. The life or efficiency of these graphitised electrodes is many times that of the same electrodes ungraphitised. I have also graphitised some tons of carbon plates, to be used in making dynamo and motor brushes, and a large variety of odd forms and sizes for divers purposes.

Another product—the one which will probably be of greatest importance—is an intimate mixture of pure amorphous carbon and graphite in fine powder. This will be put on the market for paint and foundry facing, and, as it has been formed at an extremely high temperature, it is quite pure, and possesses all of the qualities desirable for the purposes for which it is intended.

It is not the present intention of the company to enter into the manufacture of their product into finished form for the general market, but rather to encourage those who are now engaged in making up the natural graphite into articles of commerce to become buyers of their material, substituting it for that now used.

The company's plans, now being carried out, provide for the erection of a brick-and-iron building, 100 × 50 feet, on a plot of ground in Block No. 8 of the Niagara Falls Power Company's lands (adjoining the works of the Carborundum Company). Therein they will erect machinery for reducing coke to grains of the desired size, an electric furnace through which the prepared grains will pass in a continuous stream, a pulveriser for reducing the grains as received from the furnace, and a scalping sieve through which the product from the pulveriser will pass, that particles exceeding the 1/200th of an inch diameter may be removed. The final flour or powder will contain an amount of pure graphite proportionate to the percentage of impurities in the original coke. It is quite possible that, instead of using high-grade marketable coke, the fine refuse from the coke ovens—which is at present a waste material—will be utilised in the manufacture of this product.

In this connection I would call attention to the need of a specific name for the new product. *Artificial*, as applied to a product, chemically and physically identical with that made by Nature, is not pleasing: it conveys the impression that, failing to produce the real thing, a cheap imitation, a sham, is being palmed off as the genuine article. Not even the Century Dictionary's definition of artificial, as "made or contrived by art, or by human skill and labour; opposed to Nature," is sufficient to banish this feeling; for, after all, in the particular case in hand, being ignorant of the exact methods pursued by Nature, we may be simply forcing her to reveal her methods, to the final results of which we neither add nor subtract one jot or tittle. The same objections may be made to the expression *Artificial Manufacture* of Graphite, for we may not be sure that the process forced upon her is not identical with that of her own selection. *Manufactured Graphite* would be quite appropriate, were it not for the fact that it is popularly applied to articles made of graphite.

It may not detract from the general interest in this subject to call attention, in closing, to the fact that graphite, first shown to be an elementary body, an allotropic form of carbon, in the first year of the nineteenth century, is in this, the last year, made to order in great quantities, and that it will, before the close of the century, become an article of ordinary commerce in its new form. Perhaps it will take its place as the primitive form of carbon—the one it assumes under normal conditions.

METATHETIC REACTIONS BETWEEN CERTAIN SALTS IN SOLUTION IN LIQUID AMMONIA.

By E. C. FRANKLIN and C. A. KRAUS.

The great power of anhydrous ammonia as an electrolytic solvent, occupying as it does, of all known solvents, a position nearest to water in its power of dissociation (Cady, *Journ. Phys. Chem.*, 1897, i., 707) and in its capacity as a general solvent (*Amer. Chem. Journ.*, xx., 820), has led the authors to enquire whether or not metathetic reactions, similar to those which take place in aqueous solutions, do not take place also in ammonia solutions. If salts in solution in ammonia are dissociated to an extent approximating the dissociation in water solutions, then salts insoluble in ammonia should be precipitated rapidly and completely when ammonia solutions of salts containing the ions necessary for the formation of such substances are brought together. That in a considerable number of cases such action takes place is shown by the experiments described in this paper.

Method of Making the Tests.

The nitrates of sixteen metals, selected because of their ready solubility, together with the fact that they were at hand, were chosen to furnish the metallic ions, while the sulphide, chloride, bromide, iodide, chromate, and borate of ammonium constitute the list of salts which were used as precipitants.

The tests were made by bringing together in a small vacuum-jacketed test-tube solutions of the nitrate and of the precipitant, and observing whether or not a precipitate was formed.

General Results.

Ammonium Chloride as Precipitant (Table I.).—Most of the metals tested are precipitated as chlorides by the action of ammonium chloride. Those chlorides which by direct experiment were found to be entirely insoluble, separate immediately and completely when the two solutions are brought together, while those which were found to be slightly or but moderately soluble, separate slowly and incompletely from more concentrated solutions.

Ammonium Bromide as Precipitant.—Table II. gives the results obtained by the use of ammonium bromide as precipitant. As was to be expected, considering the greater solubility of the bromides, these precipitates formed more slowly than the corresponding precipitates of chlorides.

Ammonium Iodide as Precipitant (Table III.).—Corre-

sponding with the much greater general solubility of the iodides, but two metals, barium and strontium, gave precipitates with ammonium iodide, and even these, as the crystalline nature of the precipitates indicates, are probably very slightly soluble.

Ammonium Sulphide as Precipitant (Table IV.).—A solution of ammonium sulphide was prepared by passing washed and dried hydrogen sulphide into liquid ammonia. The gas dissolved, forming a clear colourless solution. Ammonium sulphide was also prepared by the action of liquid anhydrous ammonia on liquid hydrogen sulphide. To the hydrogen sulphide at the temperature of the carbon dioxide and ether bath, liquid ammonia was added, with the result that immediately a mass of white solid ammonium sulphide was formed. Excess of ammonia dissolved the solid to a clear solution. On cooling the solution, saturated at the boiling temperature of ammonia, to the temperature of the carbon dioxide and ether bath, there was an abundant separation of crystals. A small quantity of these crystals, as well as a larger quantity of the white solid, were filtered off, freed from ammonia, and transferred to a specimen tube. Although no analysis of the solid was made, there can be scarcely any doubt of its identity as ammonium sulphide.

All the metals tested, with the exception of the alkalis, gave precipitates with ammonium sulphide. Only a portion of these precipitates, however, as their most obvious property, their colour, indicates, can be identical with the precipitates formed in aqueous solutions. Certainly the lead precipitate, after removing it from the solution and drying it at the laboratory temperature, is lead sulphide. The remaining black precipitates have not been studied. The precipitates formed from barium, strontium, calcium, and magnesium solutions are especially interesting for the reason that these metals in aqueous solution give no precipitates with ammonium sulphide. It is the expectation of the authors to collect and analyse these four precipitates, but up to the present this has been accomplished in the case of but one of them, and this with not entirely satisfactory results.

Magnesium-ammonium Sulphide, $2MgS.(NH_4)_2S.xNH_3$.

Preparation.—To a Dewar test-tube containing a fairly strong solution of magnesium nitrate, an ammonia solution of ammonium sulphide was added as long as a precipitate continued to be formed. In order to separate the precipitate from the liquid, the contents of the tube were poured upon a filter, of which the following is a description. In the figure, A is the filtering funnel proper, consisting simply of a thin-walled tube of the shape and size indicated, and provided with a platinum Witt filtering plate, *b*. The filtering tube is held in place by means of corks at *c* and *d*; *e* is a vacuum-jacketed tube. The space *f* is filled with ammonia to a convenient height.

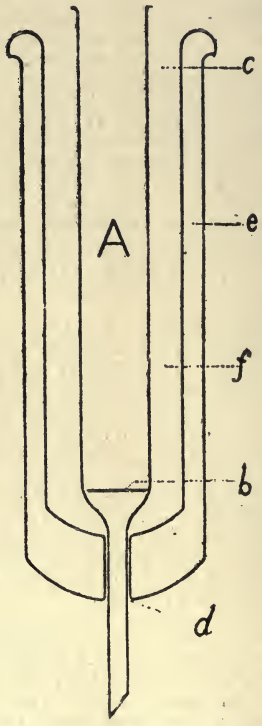
The precipitate, after being transferred to the filter, was washed several times with fresh quantities of ammonia, the filtration being accelerated by closing the mouth of the tube by means of a cork. The pressure of the supernatant gas forces the wash-fluid through rapidly. After sufficient washing, the tube was removed from the ammonia-bath, both ends were closed, one of them by means of a cork carrying a drying tube filled with soda-lime, and the ammonia allowed to pass off at the ordinary temperature.

Properties of the Precipitate.—The compound was a finely crystalline white solid, which gave off the odours of ammonia and hydrogen sulphide at the laboratory temperature. Freshly prepared, it is completely soluble in water. After standing for a short time exposed to the air, it was no longer entirely soluble—a result due undoubtedly to the formation of magnesium hydroxide by the action of the moisture and oxygen of the air.

Analysis of the Precipitate.—Portions of the compound, prepared as described above, were transferred as rapidly as possible to small weighing tubes. These were weighed and dropped into bottles containing fuming nitric acid. The sulphuric acid formed and the magnesium were determined according to the usual methods. The following results were obtained:—

	I.	II.	III.
Weight of substance	0·1691	0·1906	0·2780
Magnesium pyrophosphate.	0·1171	0·1266	0·1793
Barium sulphate..	0·3166	0·3954	0·5828
Magnesium	0·0231	0·0274	0·0387
Sulphur	0·0435	0·0537	0·0794
Per cent magnesium	13·60	14·44	13·92
,, sulphur..	25·70	28·19	28·37

These determinations, made each on a different specimen of the substance, indicate in the material analysed the presence of two atoms of magnesium to three atoms of sulphur with varying quantities of ammonia. The results obtained probably harmonise best with the assumption that the compound is a double sulphide of ammonium and magnesium, containing two molecules of magnesium



sulphide and 1 molecule of ammonium sulphide, together with ammonia of crystallisation, which, being gradually given off at temperatures above the dissociation-point of the compound, is a sufficient explanation of the variable composition as found by analysis.

The calculated percentage composition of—

$2MgS.(NH_4)_2S.9NH_3$

is—Magnesium 14·41 per cent, sulphur 28·82 per cent, ammonia 56·16 per cent; of $2MgS.(NH_4)_2S.10NH_3$ is—Magnesium 13·71 per cent, sulphur, 27·42 per cent, ammonia 58·28 per cent.

Ammonium Chromate as Precipitant (Table V.).—Chromic acid, which presumably goes into solution as ammonium chromate, dissolves sparingly. Its solution gives precipitates with all the metals tested with the exception of lithium and sodium.

Ammonium Borate as Precipitant (Table VI.).—Boracic acid, which in solution in ammonia presumably forms am-

monium borate, is but sparingly soluble. Its solution gives precipitates with all the metals tested with the exception of lithium, sodium, and potassium.

TABLE I.—*Ammonium Chloride as Precipitant.*

Salt.	Remarks.
Lithium nitrate	Precipitate, from concentrated solution.
Sodium nitrate	No precipitate.
Potassium nitrate	Precipitate, from concentrated solution.
Calcium nitrate	Precipitate, immediate.
Strontium nitrate	" "
Barium nitrate	" "
Magnesium nitrate	" "
Zinc nitrate	" "
Manganese nitrate	Precipitate, immediate, white.
Cobalt nitrate	" " "
Nickel nitrate	Precipitate, immediate, light violet.
Cadmium nitrate	Precipitate, immediate.
Mercuric nitrate	No precipitate.
Lead nitrate	Precipitate, from concentrated solution.
Silver nitrate	Precipitate, from concentrated solution.
Copper nitrate	Precipitate, from concentrated solution, blue.

TABLE II.—*Ammonium Bromide as Precipitant.*

Salt.	Remarks.
Lithium nitrate	Precipitate, from most concentrated solutions.
Sodium nitrate	No precipitate.
Potassium nitrate	No precipitate.
Calcium nitrate	Precipitate, immediate.
Strontium nitrate	Precipitate, immediate.
Barium nitrate	Precipitate, immediate.
Magnesium nitrate	Precipitate, not immediate.
Manganese nitrate	Precipitate, immediate.
Zinc nitrate	Precipitate, not immediate.
Cobalt nitrate	Precipitate, immediate, white.
Nickel nitrate	Precipitate, immediate, light violet.
Cadmium nitrate	Precipitate, immediate.
Mercuric nitrate	No precipitate.
Lead nitrate	Precipitate, from concentrated solution.
Silver nitrate	Precipitate, from concentrated solution.
Copper nitrate	Precipitate, from concentrated solution, blue.

TABLE III.—*Ammonium Iodide as Precipitant.*

Salt.	Remarks.
Lithium nitrate	No precipitate.
Sodium nitrate	No precipitate.
Potassium nitrate	No precipitate.
Calcium nitrate	No precipitate.
Strontium nitrate	Precipitate, crystalline.
Barium nitrate	Precipitate, crystalline.
Magnesium nitrate	No precipitate.
Zinc nitrate	No precipitate.
Manganese nitrate	Precipitate, slowly.
Cobalt nitrate	No precipitate.
Nickel nitrate	No precipitate.
Cadmium nitrate	Precipitate, slowly.
Mercuric nitrate	No precipitate.
Lead nitrate	No precipitate.
Silver nitrate	No precipitate.
Copper nitrate	No precipitate.

TABLE IV.—*Ammonium Sulphide as Precipitant.*

Salt.	Remarks.
Lithium nitrate	No precipitate.
Sodium nitrate	No precipitate.
Potassium nitrate	No precipitate.
Calcium nitrate	Precipitate, not immediate, white.
Strontium nitrate	Precipitate, immediate, white.
Barium nitrate	Precipitate, immediate, white.
Magnesium nitrate	Precipitate, not immediate, crystalline, white.
Zinc nitrate	Precipitate, immediate, white.
Manganese nitrate	Precipitate, immediate, white, dissolves on addition of water.
Cobalt nitrate	Precipitate pinkish, on the addition of water the precipitate turns black.
Nickel nitrate	Precipitate white, dissolves on addition of water.
Cadmium nitrate	Precipitate white, on addition of water the precipitate becomes yellow.
Mercuric nitrate	Precipitate, immediate, black.
Lead nitrate	Precipitate, immediate, black.
Silver nitrate	Precipitate, immediate, black.
Copper nitrate	Precipitate yellowish brown, from concentrated solutions.
Bismuth nitrate	Precipitate, immediate, black.

TABLE V.—*Ammonium Chromate as Precipitant.*

Salt.	Remarks.
Lithium nitrate	No precipitate.
Sodium nitrate	No precipitate.
Potassium nitrate	Precipitate, slight, flocculent.
Calcium nitrate	Precipitate, flocculent.
Strontium nitrate	
Barium nitrate	
Magnesium nitrate	
Zinc nitrate	
Manganese nitrate	
Cobalt nitrate	
Nickel nitrate	
Cadmium nitrate	
Mercuric nitrate	
Lead nitrate	
Silver nitrate	
Copper nitrate	

TABLE VI.—*Ammonium Borate as Precipitant.*

Salt.	Remarks.
Lithium nitrate	No precipitate.
Sodium nitrate	
Potassium nitrate	
Calcium nitrate	Precipitate.
Strontium nitrate	
Barium nitrate	
Magnesium nitrate	
Zinc nitrate	
Manganese nitrate	
Cobalt nitrate	
Nickel nitrate	
Cadmium nitrate	
Mercuric nitrate	
Lead nitrate	
Silver nitrate	
Copper nitrate	

—*American Chemical Journal*, xxi., No. 1.

A Common Error in Recorded Results of Proximate Plant Analysis.—Lyman F. Kebler (*Am. J. Pharm.*, lxxi., 25).—The author calls attention to the error caused by adding the percentage of ash to the percentage of the other constituents instead of estimating it in the dried residue left after the action of the various solvents.

A NEW COMMERCIAL METHOD FOR THE MANUFACTURE OF TARTARIC ACID.

By Dr. G. SCARLATA.

TARTARIC acid occupies one of the most important places among chemical products. It is found in abundance in the form of acid tartrate of potassium and neutral tartrate of lime, in the raw tartar from casks, in wine lees, and in grape skins, which, by the way, constitute the only raw materials used for its extraction.

It is curious to note that, at the present time, the extraction of tartaric acid is almost entirely carried on in England, the United States, and Germany, the wine-producing countries possessing only a few factories of little importance, limited to the treatment of raw material produced on the spot, though more often—in fact nearly always—the stocks are allowed to accumulate, and are then shipped to some foreign factory.

The method of extraction at present used in most factories is very old, viz., that of Scheele. Only very slight modifications have been introduced into this method, while nearly every other chemical industry has undergone radical changes; one fact is certain, that there has been no improvement made in the manufacture of tartaric acid.

I have been attracted to this remunerative industry with the hope of devising a plan by which the English and German methods can be efficiently combined. I have therefore sought principally for an economical method which would not require too much capital to establish in the first place.

The results I have obtained in the laboratory lead me to hope that I have attained the desired result. I leave to practical experience the task of justifiying my opinions.

The first part of Scheele's process consists in obtaining tartrate of calcium. This can be done by different methods, but they are all long and delicate. The methods of Scheurer-Kestner, of Gladysz, of Dietrich, and of Schutzner, all require a considerable amount of time and fuel; the same can be said of the second part of the process, which consists of decomposing the tartrate of calcium with sulphuric acid. This operation yields no useful by-product, and does not allow of the recovery of any of the materials first used.

These drawbacks do not exist in the new method which I propose to use, since by its means we are enabled to extract the tartaric acid directly from the raw product, and to recover the materials used in the operation.

This method, broadly speaking, is based on the decomposition of the tartrates by fluosilicic acid. In the raw product the tartaric acid exists both as acid tartrate of potassium and as tartrate of calcium. These salts are decomposed by fluosilicic acid, with the formation of tartaric acid and of the corresponding fluosilicates.

$$2C_4H_5O_6K + H_2SiFl_6 = 2C_4H_6O_6 + K_2SiFl_6$$
$$C_4H_4O_6Ca + H_2SiFl_6 = C_4H_6O_6 + CaSiFl_6.$$

Tartaric acid and fluosilicate of calcium are both soluble and remain in the clear solution, while the fluosilicate of potassium is to a great extent precipitated; its solubility is only 1 part in 825 parts of water. By evaporating the clear solution the last portions of the fluosilicate of potassium are precipitated very rapidly. There now remains only the fluosilicate of calcium to be eliminated, of which the quantity present is first determined by analysis. The calculated quantity of sulphuric acid is then added, plus a little excess, as tartaric acid crystallises much better in solutions made slightly acid with sulphuric acid. After concentration to help the deposit of sulphate of lime, the organic matter, and the last traces of fluosilicate of potassium, the clear solution is decanted and allowed to crystallise.

We thus obtain fluosilicate of potash as principal by-product; it is found mixed with silica for reasons which will be shown later on, and constitutes an excellent material for the preparation of fluosilicic acid; in fact, by treating it with sulphuric acid, we obtain sulphate of potassium, hydrofluoric acid, and fluoride of silicon, according to the equation—

$$K_2SiFl_6 + H_2SO_4 = SiFl_4 + 2HFl + K_2SO_4.$$

But hydrofluoric acid in the presence of silica gives fluoride of silica and water:—

$$4HFl + SiO_2 = SiFl_4 + 2H_2O.$$

So that the whole of the fluorine from the fluosilicate of potassium is brought to the state of fluoride of silica, which, by reacting on water, gives fluosilicic acid and silica according to the equation—

$$3SiFl_4 + 4H_2O = 2H_2SiFl_4 + Si(OH)_4.$$

As can be seen, the recovery of the fluosilicic acid is complete by a simple treatment with sulphuric acid.

Preparation of Tartaric Acid.

I am not able to describe in detail the apparatus necessary for the manufacture of tartaric acid, but will confine myself to the description of the experiments made with the ordinary apparatus found in the laboratory.

The tartar I used contained by analysis:—

Total tartaric acid	62·56	per cent.
Tartrate of potassium ..	67·16	,,
Tartrate of calcium.. ..	11·25	,,

I operated on 10 kilogrms. of well broken-up material, placed in a wooden vat furnished with a stirrer. To these 10 kilogrms. of raw material I added the quantity of fluosilicic acid theoretically necessary to set all the tartaric acid at liberty,—that is to say, 58 kilogrms. of a solution at 60 per cent. After agitating for an hour, the mixture was transferred to a filter-press, and the clear solution was led into a wooden vat lined with lead and heated by a current of steam passing through a spiral tube. The evaporation was continued until fluosilicate of potassium commenced to be deposited. The contents of the vat were then left alone for some hours, after which the clear solution was decanted into another vat furnished with a stirrer. The lime was estimated on a sample of the solution, by adding an excess of oxalate of ammonia and titrating the excess of oxalic acid by permanganate of potash. The total quantity of solution contained 209 grms. of lime. To eliminate this the solution was treated with the theoretical quantity of sulphuric acid,—that is 512 grms. H_2SO_4 diluted to 1 litre, then transferred to the filter-press.

The solution of tartaric acid thus obtained was coloured a deep reddish brown; after decolourising by animal-black, it was evaporated and crystallised, care being taken to remove the sulphate of lime which is again precipitated at the commencement of the evaporation.

The purity of the crystals of tartaric acid thus obtained was determined by titrating with potash and comparing it with a chemically pure sample of the same acid. It is evident that, in this kind of test, equality of results indicates equality of purity. The results obtained were as follows:—

Tartaric acid at 100 per cent.

I.	35·0	c.c. of	solution of KOH.
II.	41·0	,,	,, ,,
III.	33·0	,,	,, ,,
IV.	36·0	,,	,, ,,

Tartaric acid from the experiment.

I.	34·5	c.c. of	solution of	KOH.
II.	40·5	,,	,,	,,
III.	32·5	,,	,,	,,
IV.	35·5	,,	,,	,,

These figures show that the tartaric acid obtained by the fluosilicic acid process titrated 98·57 per cent of purity; it may therefore be considered as commercially pure.

Preparation of the Fluosilicic Acid necessary for the Operation.

Description of the Apparatus.—This consists of a cast-iron pot fitted with a mechanical stirrer, in which the raw

material obtained as a by-product from the above reaction is placed. The calculated quantity of concentrated sulphuric acid is added, the cover is luted on, and the whole heated and stirred continuously. The cover has two tubes passing through it; the first—which is for passing a current of air through at the end of the operation—is kept closed by means of a tap during the first phase of the operation; the second—which is much larger—is for the purpose of passing the fluoride of silicon into a vessel filled with water. The water necessary for the decomposition of the fluoride of silicon is added, the quantity is estimated approximately by the quantity of fluosilicate of potash present, so that the solution of fluosilicic acid can be prepared of practically any desired strength. The fluoride of silicon, on entering the vessel, comes in contact with the water, which decomposes it into fluosilicic acid and gelatinous silica.

As a secondary product of this preparation, we obtain sulphate of potassium, which, mixed with the residues from the first operation, forms excellent manure. In any case its intrinsic value will always cover a part of the expense of the process.

As can be seen, this method has the double advantage of being very rapid, and of returning in a useful form all the materials originally used. — *Moniteur Scientifique*, Series 4, vol. xiii., May, 1899.

ON THE DOUBLE CHLORIDES AND BROMIDES OF URANIUM.

By J. ALOY.

Double Alkaline Uranous Chlorides.

Both the uranous chloride, UCl_4, and the uranous bromide, UBr_4, have a strong tendency to unite with the chlorides and bromides of the other metals. Nevertheless the only compound of this order known up to the present was the double chloride of uranium and sodium, $UCl_4.2NaCl$, by the use of which M. Moissan was enabled to obtain pure metallic uranium (*Comp. Rend.* cxxii., 1089). This compound is prepared by the direct action of the vapours of uranous chloride on melted chloride of sodium at a dull red heat. I have, in the same manner, prepared compounds of uranous chloride from the chlorides of potassium and lithium. The experiment is carried out in a Bohemian glass tube in a laboratory gas furnace; the uranous chloride is produced at one end of the tube by the action of chlorine on carbide of uranium, and then passed over the well-dried alkaline chloride placed in a series of boats, heated to dull redness. Under these conditions the chloride, UCl_4, combines with the alkaline chloride contained in the first of these boats, and soon the mass melts by reason of the formation of the double chloride; the action then spreads successively to the other boats.

We could, in this experiment, replace the carbide of uranium by a mixture of oxide of uranium and carbon; it would, however, in such a case, be necessary to greatly increase the temperature of the mixture, and therefore use a very hard, and well protected glass tube.

Whatever the method of preparation, the compounds thus formed correspond to the formulæ $UCl_4.2KCl$ and $UCl_4.2LiCl$.

In appearance they differ but slightly from the double chloride of sodium and uranium described by M. Moissan.

Coloured pale green at the moment of their formation, they soon become dark green on contact with the air from which they absorb the moisture. Much more stable than uranous chloride, these double chlorides, are, however, very greedy for water; their solution, of a beautiful green colour, is effected with a rise of temperature, and possesses a strongly acid reaction.

When very dilute and gently heated, this solution becomes brown like that of uranous chloride; it oxidises slowly in the air, and it requires several days for the oxidation to be complete. Evaporated *in vacuo* over sulphuric acid, it deposits, even in the presence of an excess of uranous chlorides, crystals of alkaline chloride and an uncrystallisable green mass soluble in water. This result, which is due to the dissociation of the compound by water with the liberation of hydrochloric acid, explains the want of success of some chemists who have tried to prepare the pure double chlorides by mixing the two component parts. Ordinary alcohol also exercises a dissociating action, and gives a green solution, which quickly becomes yellow while oxidising; when exposed to sunlight, this solution rapidly becomes brown. The double alkaline uranous chlorides are very soluble in acetic acid.

Double Alkaline-earthy Uranous Chlorides.

The alkaline-earthy chlorides also possess the property of uniting, under the same conditions, with uranous chloride. But the experiment always requires certain precautions; it is necessary, in order to obtain a definite compound, to thoroughly dry the chlorides in a current of dry hydrochloric acid, and not to raise the temperature of the boats to too high a point: by proceeding in this manner the uranous chloride unites with the alkaline-earthy chlorides, giving a fusible compound corresponding to the formula $UCl_4.M''Cl_2$, where M'' represents the alkaline-earthy metal: barium, strontium, calcium.

These double chlorides possess a deeper green colouration than that of the corresponding alkaline chlorides.

In the same manner as these latter they are dissociated by water, and will not crystallise in a dry vacuum.

Double Uranous Bromides.

Uranous bromide, UBr_4, also forms double bromides with the alkaline bromides. I have obtained compounds of potassium and sodium by acting on the alkaline bromide, heated to redness by vapour of uranous bromide.

The bromide, UBr_4, is produced by the action of pure bromine, very carefully dried by means of chloride of calcium, on a mixture of equal parts of green oxide of uranium and carbon. The experiment is made in a porcelain tube heated to bright redness, or in a very hard glass tube, well protected at the part containing the mixture; the bromine is carried in by a current of dry carbonic acid; as soon as the fumes of uranous bromide appear the currrent of gas is increased, the bromine combines with the alkaline bromide which it colours; the mass then melts, and, if the experiment is sufficiently prolonged, the compounds produced correspond to the formulæ $UBr_4.2KBr$ and $UBr_4.2NaBr$. These bromides are of a deeper green than the corresponding chlorides, and possess analogous properties.

In these experiments I was not able to make use of carbide of uranium, which decomposes carbonic acid, giving uranic oxide.

The alkaline-earthy bromides of barium, calcium, and strontium also combine with uranous bromide.

Double Subchlorides of Uranium.

The double subchlorides of uranium and the alkaline metals which have up to the present only been prepared in the wet way, can also be obtained by direct action. By passing a current of dry chlorine over gently heated protoxide of uranium, we obtain the subchloride of uranium; if we increase the temperature as soon as the transformation of the oxide is complete, and increase the current of chlorine, the subchloride of uranium can be carried over and combined with the alkaline chlorides, with which they give fusible compounds of a beautiful golden-yellow colour, the study of which I am pursuing. In a forthcoming paper I shall complete the history of these compounds, and describe some other complex compounds of uranium. — *Bull. Soc. Chim.*, Series 6, vol. xxi., No. 6.

ON CHLORATED EXPLOSIVES.

By BERGÈS CORBIN.

THE method of manufacturing explosives described in this paper consists in mixing the chlorate with nitrated or nitric derivatives dissolved in certain oils.

Picro-naphthalene, for example, is prepared by gradually adding 1·320 kilos. of picric acid, in small portions at a time, to 1 kilo. of melted mononitro-naphthalene. The compound thus obtained melts at 74° C., and dissolves in castor oil in the proportion of 5 per cent in the cold and 80 per cent when warmed (100° C.). At 105° to 110°, 20 grms. of castor oil will dissolve as much as 20 or 30 grms. of this substance.

Picro-nitrobenzene, which is prepared in an analogous manner, melts at 88° and dissolves in castor oil in the following proportions:—

6 to 7 per cent	.. ..	In the cold.
40 ,,	.. ..	At 100°.
100 ,,	.. ..	Above 100°.

The picrates of amidoazobenzene, azobenzene, azoxybenzene, as well as the picrates of the nitrodiphenylamines, have practically the same solubilities in castor oil as the azo-derivatives from which they were formed. The picro-azoic derivatives are obtained by dissolving the nitro-compounds in castor oil at 80° to 100°, and gradually adding picric acid. The solutions thus obtained may be heated well above the temperature at which the nitric derivatives used decompose. Even at 200° no explosion occurs, neither are they decomposed. As a general rule the picric acid can be replaced by picramic acid.

In a similar manner we can prepare compounds containing nitrobenzene and the nitronaphthalenes, and, thanks to the presence of the first of these bodies, we can dissolve a larger proportion of the second in oil; for example, 20 grms. of an animal or vegetable oil will, in the cold, only dissolve 5 grms. of nitronaphthalene, while 10 grms. of the same oil containing 10 grms. of nitrobenzene will dissolve 10 grms. of nitronaphthalene.

To prepare chlorated explosives, the simple or mixed nitrated or nitric derivatives are dissolved in a suitable oil, gradually heated, and the solution mixed with powdered starch or wood charcoal, if one of these substances is required; finally, the chlorate or perchlorate is added in small portions at a time, and the mixing continued until the mass is perfectly homogeneous.—*Zeit. Angew. Chem.*, 1898, xlvii., 1091.

THE ELECTROLYSIS OF ALKALINE CHLORIDES.

By H. WOHLWILL.

THE author, considering chloride of sodium to be typical of the alkaline chlorides, selected it for studying its decomposition by electrolysis.

Besides the usual formation of caustic alkali at the cathode, and of chlorine at the anode, we know that certain other reactions take place during the course of the electrolysis, reactions which give rise to the formation of oxygenated acid salts of chlorine. The principal of these salts are the hypochlorites, the chlorates, and—under certain peculiar conditions—the perchlorates.

A question which has both a practical and theoretical interest is that of knowing how a solution originally containing only the anions $\overline{Cl}$, $\overline{OH}$ and O, becomes charged with the constitutive anions of the hypochlorites and the chlorates,—that is to say, $\overline{ClO}$ and $\overline{ClO_3}$.

In order to solve this problem, the author has adopted the experimental method proposed by Glaser for studying the electrolysis of aqueous solutions in general. The same problem has been attacked by Oettel and indirectly by Haber; but the intention of the author being to isolate the primary reactions, he took the precautions necessary for observing the initial tendency of these reactions, and not the ultimate products of the electrolysis, as was done by Oettel and Haber.

According to the author, the principal objections which can be made to the methods of his predecessors are the following:—The duration of the experiment is too long; the products of the electrolysis are not separated one from the other, and consequently may be further affected by the current; the composition and concentration of the liquid are essentially variable; &c. By removing these unfavourable conditions, by which simply the sum of the different reactions are given, without allowing any particular one to be characterised, the author has arrived at the following conclusions:—

1. With an electromotive force not exceeding 1·2 volts, a hypochlorite is formed; with an electromotive force of from 1·2 to 1·3 volts, the reaction is almost quantitative, apparently according to the equation—

$$Cl + \overline{O}\ (++) = \overline{ClO}.$$

2. Above 2·1 volts the formation of the hypochlorite is more accentuated on account of the secondary reaction of the liberated chlorine on the alkali present.

3. The chlorate is formed by the reaction of ions susceptible of furnishing positive electricity,* and not by the direct union of the ions $\overline{Cl}$ and $\overline{HO}$, as was admitted by Haber. It is much more probable that the reaction is expressed by the formula—

$$2\overline{ClO} + \overline{OH}\ (++) = ClO_3H + \overline{Cl},$$

in which ClO represents the ions of the hypochlorous acid already formed in the solution.—*Zeits. f. Elektrochemie*, v. (5), p. 52.

ON A NEW METHOD OF FORMING CUPROUS CYANIDE.

By HENRI VITTENET.

WE heat a mixture of—

Neutral acetate of copper	.. .. ..	15 grms.
Ammonia at 21° B.	.. ..	30 ,,

in a sealed tube for two hours at a temperature of 180—185°.

The solution is almost entirely decoloured, and carries in suspension a mixture of very fine spangles of metallic copper and of opaque white crystalline flakes. On opening the tube no pressure was noticed. We filtered on a filter-pump; the liquid immediately took a blue colour. The precipitate was washed on the filter with distilled water until it entirely lost its blue colour, and was then digested with water slightly acidulated with H_2SO_4, so as to dissolve the metallic copper.

There thus remained the opaque white flakes, which, when heated to redness on a sheet of platinum, gave a red deposit of copper; they are soluble in boiling dilute hydrochloric acid, in cyanide of potassium, insoluble in dilute boiling sulphuric acid, soluble in nitric acid (giving a green liquid), soluble in concentrated boiling ammonia (giving a blue solution). They give off ammonia when calcined with soda-lime. In short, we have identified this body with the cuprous cyanide obtained by precipitation by adding a hydrochloric solution of cuprous chloride to a solution of cyanide of potassium.

* The expressions *positive* and *negative* electricity, which had completely disappeared from scientific language, have been revived by German electrochemists following the work of Arrhenius on electrical dissociation. They are further in harmony with the modern theories of electrolysis.

Analysis has given the following results:—

I. Material taken, 0·3064 grm.

Water	0·112 grm.
CO_2	0·1475 ,,
CuO	0·2674 ,,

II. Material taken, 0·2185 grm.

N .. .. .. 29 c.c. at 19°, 763·35 m.m.

Or in parts per cent—

	Found. I.	Found. II.	Calculated for $Cu_2C_2N_2$.
C	13·12	—	13·48
H	0·40	—	0·00
Cu	69·79	—	70·78
N	—	15·27	15·73

The blue liquid resulting from the reaction is treated with 100 c.c. of alcohol at 93°, and set to crystallise in the cold under an exsiccator. It deposits blue needles, which give all the reactions of carbonate of copper.

The cyanogen group is formed by the union of the ammoniacal nitrogen and the carbon of the acetic acid.

The theoretical equation is difficult to express in view of the copper and carbonate of copper mentioned. Doubtless other unnoticed products were formed at the same time.—*Bull. Soc. Chim.*, Series 3, xxi., No. 6.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during this month shows a considerable deficit; the actual fall has been 1·37 inches, spread over 11 days; the average fall for May is 1·83 inches, making a deficit of 0·46 inch; this brings the deficit for the year to 0·69 inch, or 7·7 per cent on the thirty years' average.

Our bacteriological examinations of 382 samples have given the results recorded in the following table; we have also examined 40 other samples, from special wells, standpipes, &c., making a total of 422 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	430
New River, filtered (mean of 77 samples) ..	15
Thames, unfiltered (mean of 26 samples) ..	3247
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 201 samples)	26
Ditto ditto .. .. highest	202
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	1313
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	11

The water supply still remains in the same satisfactory condition as it was last month, when we said it was of exceptional microbic purity.

The number of analyses made in connection with former reports have reached a total per month of 182, but it will be observed that our present report deals with 208, or an additional number of 26 samples. Moreover, we have examined bacteriologically 422 samples, against an average of 292 samples in former months; showing an increase of 130. Our object in thus increasing the number of samples examined has been to meet the objection occasionally urged, that there were certain districts of London not served by special branch works or clear water wells from which we took the samples. By the inclusion of the additional samples taken from other districts named in the accompanying tables, we believe the whole of the water supply of the Metropolis is now substantially under examination as it is delivered into the mains of the respective Companies.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY CONVERSAZIONE.

June 21st, 1899.

A MOST brilliant and enjoyable *conversazione* was held at the Royal Society's Rooms, Burlington House, on Wednesday evening last. Owing to the unfortunate indisposition of Lord Lister, the guests and Fellows were received by Lord and Lady Kelvin. Among the many and varied exhibits the most interesting were:—

An apparatus shown by Mr. Mackenzie Davidson, M.B., by means of which Röntgen ray shadows could be seen in spectroscopic relief.

Experiments on the hissing of the electric arc were given by Mrs. Ayrton. On gradually increasing the current through an arc maintained between carbons at a fixed distance apart, a point is reached when the arc hisses, its appearance changes, and the electric pressure falls about 10 volts. The experiments show that this happens when the crater is too large to occupy the end only of the positive carbon, and therefore extends up its side. The crater, being no longer protected by carbon vapour from coming into direct contact with the air, now burns instead of volatilising, and it is this burning which causes hissing with its accompanying phenomena. This is proved (1) by excluding air from the arc, when experiment shows that the current can be increased, without producing hissing, to several times the value that would cause hissing in air; (2) by blowing air, or oxygen, down a tubed positive carbon, when hissing is found to take place even with quite a small current.

Experiments showing the manufacture of tubes from rock crystal in the oxy-hydrogen blowpipe flame by Mr W. A. Shenstone and Mr. W. T. Evans. Tubes of 1

centimetre in diameter, composed of rock crystal, can now be made of considerable length at the rate of about 3 centimetres an hour.

Dr. Allan Macfadyen also showed some interesting cultures and microscopical slides of certain pathogenic bacteria, such as, for example, typhoid, cholera, plague, diphtheria, &c.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 21, May 23, 1899.

New Compounds of Camphor with Aldehydes.—A. Haller.—The new compounds described in this paper are prepared by the action of piperonal and meta- and para-methoxybenzoic aldehydes on sodium camphor. These compounds of the aldehyde derivatives are easily reduced to alcoholic compounds. The reduction, instead of beginning on the group CO, as is the case with camphor, starts first on the non-saturated carbon group, C=C, then on the carbonyl group.

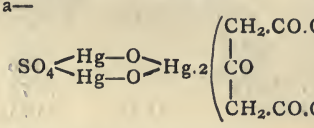
Action of Sulphuretted Hydrogen on Silicates.—P. Didier.—At a high temperature, hydrogen sulphide acts on the greater number of silicates and transforms them partially into sulphides. The author examines the cause of this reaction and the secondary reactions which accompany it for a certain number of minerals. The experiments are conducted in a porcelain tube at about 1400°, with a porcelain or carbon boat. In the greater number of experiments a small quantity of sulphuric acid is produced as a secondary reaction, which is found in the cold part of the tube. The displaced silica either is found free or else it forms silicates more acid than the original compound. The silica is not crystalline.

Di-isoamylacetic Acid.—H. Fournier.—The author prepared synthetically di-isoamylacetic acid by decomposing by heat di-isoamylmalonic acid, $(C_5H_{11})_2C(COOH)_2$. The latter acid was heated in an oil-bath to a temperature a little above its fusion-point. Carbonic acid began to be evolved at about 150°, and came off rapidly at 160°. The temperature was slowly raised to 175°, when the whole was cooled and the di-isoamylacetic acid extracted with alcohol. The acid thus prepared was in the form of white needle-shaped crystals, melting at 46—47°, insoluble in water, very soluble in ether, alcohol, carbon disulphide, and benzene. The acid was transformed into di-isoamylacetamide, $(C_5H_{11})_2CH—CONH_2$, by heating it with half its weight of phosphorus trichloride at 100° for half an hour. The resulting liquid is poured drop by drop into strong ammonia solution, and cooled by a freezing mixture. The crystals were washed with water and crystallised from alcohol.

Fluorine in Mineral Waters.—Charles Lepierre.—There exist certain mineral waters, very rare it is true, which are relatively very rich in fluorine. The most interesting example—perhaps unique in Europe—is that of the mineral waters of Gerez (North of Portugal). The author's analysis shows there to be 22 to 25 m.grms. of alkaline fluoride (probably sodium) per litre, which amounts to 10 to 12 m.grms. of combined fluorine. It is enough to evaporate half a litre of Gerez water in a platinum dish to discover positively the existence of fluorides in the residue. The analytical detection of fluorine in the waters can be made—(1) By the ordinary method of heating the residue from the water with sulphuric acid and showing the corrosion of glass; (2) by Lannes' or Carnot's method; (3) if silica is present, by the formation of SiF_4; (4) by the formation of crystals of fluosilicate of sodium, of which the little hexagonal prisms are characteristic. This last reaction is very sensitive.

Bulletin des Travaux de la Société de Pharmacie de Bordeaux. April, 1899.

Acetone Dicarbonic Acid: a Product of the Manganic Oxidation of Citric Acid.—G. Denigès.—The author found that acetone-dicarbonic acid gave with mercuric bisulphate a compound corresponding to the formula—



This compound was obtained by boiling 100 c.c. of the sulphate of mercury reagent (prepared by dissolving 5 grms. of red or yellow mercuric oxide in a warm mixture of 20 c.c. of sulphuric acid and 100 c.c. of water) and, *immediately on removing from the fire*, adding a *cold* solution of 1 grm. of acetone-dicarbonic acid in 125 c.c. of water. The abundant white precipitate is allowed to settle, washed by decantation, and filtered; it is then dried, first on porous plates, then over concentrated sulphuric acid. Analysis gives:—

	Found.	Calculated for $SO_4Hg.2HgO.2(C_5H_4O_5Hg)$.
Hg (per cent)	70·25	70·62
SO_4H_2 ,, ...	6·97	6·92
C ,, ...	8·12	8·48
H ,, ...	0·65	0·56

It is a white substance, soluble in hydrochloric acid, insoluble in water. The author shows that it is identical with the compound given by sulphate of mercury with the products of the manganic oxidation of citric acid.

On a very Sensitive Reaction of Acetone-dicarbonic Acid.—G. Denigès.—To detect the presence of very small quantities of this acid, we add to the solution under examination one-tenth of its volume of the mercuric reagent and stir well. The reaction is never instantaneous, but after a short interval—perhaps even some minutes, if only a few m.grms. per litre are present—a white cloudiness is suddenly formed, quickly followed by a precipitate if the proportion of acid present reaches some centigrms. per cent. With solutions containing at least 5 centigrms. of acid per litre, the characteristic cloudiness is obtained before the liquid boils, and, in the case of very concentrated solutions, almost immediately on mixing. With only 2 m.grms. per litre, the sudden cloudiness only appears fifteen or twenty minutes after the boiling-point has been reached and the tube withdrawn from the flame. The approximate estimation of acetone-dicarbonic acid can be easily made by chronometric means, by adding 0·5 c.c. of the mercuric reagent to 5 c.c. of the solution under examination and noting the exact number of seconds before the cloudiness appears, and referring to a table here given.

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THE CHEMICAL NEWS.

Vol. LXXIX., No. 2066.

ON THE COMPARATIVE EFFICIENCY AS CONDENSATION NUCLEI OF POSITIVELY AND NEGATIVELY CHARGED IONS.*

By C. T. R. WILSON, M.A.

The experiments described in this paper were undertaken with the object of throwing some light upon what appeared to be fundamental questions in connection with the electrical effects of precipitation. It was hoped in this way to make some advance towards an understanding of the relation between rain and atmospheric electricity.

It was pointed out by Professor J. J. Thomson (*Phil. Mag.*, December, 1898) that if positive and negative ions differed in their power of condensing water around them, drops might be formed upon one set of ions only, and separation of positive and negative electricity would then take place by the falling of the drops, the work required for the production of the electric field being due to gravity.

To make this process worthy of consideration as a possible source of atmospheric electricity, it would be necessary to show reason for believing (1) that atmospheric air in the regions in which rain is formed is likely to contain free ions, (2) that positively and negatively charged ions differ in their efficiency as condensation nuclei.

It is mainly with the second of these questions that this paper deals. The result of this part of the investigation was to prove that water condenses much more readily on negative than on positive ions. The experiments consisted in measurements of the expansion required to cause condensation in the form of drops in air initially saturated and containing ions, alternately nearly all positive and nearly all negative. The ratio of the final to the initial volume being indicated by v_2/v_1, then to cause water to condense on negatively charged ions, the supersaturation must reach the limit corresponding to the expansion, $v_2/v_1 = 1{\cdot}25$ (approximately a fourfold supersaturation). To make water condense on positively charged ions, the supersaturation must reach the much higher limit, corresponding to the expansion $v_2/v_1 = 1{\cdot}31$ (the supersaturation being then nearly sixfold).

We see, then, that if ions ever act as condensation nuclei in the atmosphere, it must be mainly or solely the negative ones which do so, and thus a preponderance of negative electricity will be carried down by precipitation to the earth's surface.

Incidentally it was proved that the difference between the effects as condensation nuclei of the positively and negatively charged ions is not to be explained by supposing that the charge carried by the negative ions is, say, twice as great as that carried by the positive ions, for equal numbers of positive and negative ions are produced by the ionisation of the neutral gas.

Attempts were now made to find an answer to the first question suggested above—Is there any evidence that ions are likely to be present under normal conditions in the atmosphere?

Former experiments furnished a certain amount of evidence in favour of an affirmative answer.

When moist dust-free air is allowed to expand suddenly a rain-like condensation always takes place if the maximum supersaturation exceeds a certain limit. This limit is identical with that required to make water condense on ions; the identity is in fact so exact as to furnish what is at first sight almost convincing evidence that ordinary moist air is always to a very slight extent ionised. The number of these nuclei is too small to make the absence of sensible electrical conductivity in air under ordinary conditions inconsistent with the view that they are ions.

All attempts, however, to remove these nuclei, by applying a strong electric field such as would have removed ordinary ions almost as fast as they were produced, have failed, even when a differential apparatus was used such as would have made manifest even a slight diminution in the number of the nuclei by the action of the field. The same is true of the similar nuclei produced by the action of weak ultra-violet light on moist air.

Such nuclei, therefore, in spite of their identity as condensation nuclei with the ions, cannot be regarded as free ions, unless we suppose the ionisation to be developed by the process of producing the supersaturation. This question requires further investigation.

* Abstract of a Paper read before the Royal Society, June 15, 1899.

A COMPARISON OF PLATINUM AND GAS THERMOMETERS, INCLUDING A DETERMINATION OF THE BOILING-POINT OF SULPHUR ON THE NITROGEN SCALE:

An Account of Experiments made in the Laboratory of the Bureau International des Poids et Mesures, at Sevres.*

By Drs. J. A. HARKER and P. CHAPPUIS.

In 1886 Professor Callendar drew attention to the method of measuring temperature, based on the determination of the electrical resistance of a platinum wire. He showed that the method was capable of a very general application, and that the platinum resistance thermometer was an instrument giving consistent and accurate results over a very wide temperature range.

Callendar pointed out that if R_0 denote the resistance of the spiral of a particular platinum thermometer at 0°, and R_1 its resistance at 100°, we may establish for the particular wire a temperature scale, which we may call *the scale of platinum temperatures*, such that if R be the resistance at any temperature T°, this temperature on the platinum scale will be—

$$\frac{R}{R_1 - R_0} \times 100 \text{ degrees.}$$

For this quantity Callendar employs the symbol pt, its value depending on the sample of platinum chosen.

In order to reduce to the standard scale of temperature the indications of any platinum thermometer, it is necessary to know the law connecting T and pt. These are, of course, identical at 0° and 100°, but the determination of the curve expressing the relationship between them is a matter for experiment.

The work of Callendar had established for a particular sample of platinum the relation—

$$d = T - pt = \delta\left[\left(\frac{T}{100}\right)^2 - \frac{T}{100}\right]$$

over the range 0° to 600°, T being measured on the constant pressure air scale.

Later experiments by Callendar and Griffiths showed that this relation holds for platinum wires generally, provided they are not very impure. They propose that the value of δ, the constant employed in the formula, should be determined by taking the resistance of the thermometer in the vapour of sulphur. A new determination of this point on the air scale made by them gave 444·53° as the boiling-point under 760 m.m. pressure.

* Abstract of a Paper read before the Royal Society, June 15, 1899.

The present paper is the outcome of the co-operation of the Kew Observatory Committee and the authorities of the International Bureau of Weights and Measures at Sèvres, for the purpose of carrying out a comparison of some platinum thermometers with the recognised international standards.

A new resistance-box, designed for this work, and special platinum thermometers, together with the other accessories needed, were constructed for the Kew Committee, and, after their working had been tested at Kew, were set up at the laboratory at Sèvres, in August, 1897. The comparisons executed between these instruments and the standards of the Bureau may be divided into several groups. The first group of experiments covers the range −23° to 80°, and consists of direct comparisons between each platinum thermometer and the primary mercury standards of the Bureau. Above 80° the mercury thermometers were replaced by a gas-thermometer, constructed for measurements up to high temperatures. The comparisons between 80° and 200° were made in a vertical bath of stirred oil, heated by different liquids boiling under varying pressures. For work above 200° a bath of mixed nitrates of potash and soda was substituted for the oil tank. In this bath comparisons of the two principal platinum thermometers with the gas-thermometer were made up to 460°; and with a third thermometer, which was provided with a porcelain tube, we were able to go up to 590°. Comparisons of the platinum and gas-scales were carried out at over 150 different points, each comparison consisting of either ten or twenty readings of the different instruments.

By the intermediary of the platinum thermometers a determination of the boiling-point of sulphur on the nitrogen scale was also made. The mean of three very concordant sets of determinations with the different thermometers gave 445·27° as the boiling-point on the scale of the constant volume nitrogen thermometer, a value differing only 0·7° from that found by Callendar and Griffiths for the same temperature expressed on the constant pressure air scale.

If for the reduction of the platinum temperatures in our comparisons we adopt the parabolic formula, and the value of δ obtained by assuming our new number for the sulphur-point, we find that below 100° the differences between the observed values on the nitrogen scale and those deduced from the platinum thermometer are exceedingly small, and that even at the highest temperatures the differences only amount to a few tenths of a degree.

Full details as to the instruments employed and the methods adopted are given in the paper.

ON SOME PHOTOGRAPHIC PHENOMENA CONNECTED WITH THE COLSON-RUSSELL EFFECT.

By J. H. VINCENT, D.Sc. (Lond.), A.R.C.Sc.

Introduction.

Colson, who has for several years been publishing papers on the effects of various agents on a photographic plate, first found that heat in presence of moisture from paper, &c., was able to so affect a photographic plate as to cause a darkening of the sensitive surface when the plate was treated with a developer (*Comptes Rendus*, Jan., 1896, cxxii., 598—600). Colson subsequently found that the air in the neighbourhood of some bright metals possessed a similar property (*Comptes Rendus*, Jan., 1896, cxxiii., 49—51). This he attributed to the action of the vapours of the metals themselves.

Russell discovered both these effects quite independently a little later, and in a series of papers (Chemical News, lxxv., 302; 1898, lxxvii., 167; *Proc. Roy. Soc.*, xiii., 102; lxiv., 409) has shown that both classes of effect are probably due to the same active agent. This agent is, in his opinion, hydrogen peroxide, and he has obtained chemical tests for the presence of this body in all cases in which the plate has been darkened by the emanations under discussion. The chemical recognition of hydrogen peroxide is a matter of great difficulty and uncertainty, and the probability of the truth of Russell's theory rests more securely on the perfect analogy which he has shown to exist between the behaviour of the vapours from active bodies and that of hydrogen peroxide. The completeness with which this similarity in properties is exhibited is remarkable, and can hardly be capable of any other interpretation than that of the identity of the active agents.

It must be borne in mind, however, that another explanation of the photographic activity of metals like zinc has been put forward by von Lengyel (*Wied. Ann.*, 1898, lxvi., [5], pp. 1162-1170), who looks upon hydrogen as the active agent. According to this author, hydrogen has an effect on a photographic plate similar to that of light, producing a modification of silver bromide which is reduced by an ordinary developer. Russell, however, states in his first paper that in an atmosphere of hydrogen the action takes place as in ordinary air. This means that the effect of the hydrogen itself was so slight as not to be noticed by Russell, in comparison with the effect of the active bodies he was investigating.

The work of Russell shows that the dry plate furnishes a means to distinguish between hydrogen peroxide and ozone, as the latter does not affect the film. But in making use of this test the action of ozone upon any substance in the neighbourhood of the plate must be considered. It is the object of this paper to show that some bodies, which, although perfectly inactive previously, become strongly active when treated with even small quantities of ozone.

Experiments with Indiarubber.

Indiarubber, as Russell has proved, is an inactive substance. That is to say, it may be put in contact with a photographic dry plate for a week or so without exerting any effect on the plate capable of causing darkening on development. But if ozonised air be allowed to come into contact with the rubber for only a short time, it becomes so active as to give a picture in a few minutes. The effect may be heightened by passing the ozonised air over the indiarubber in a gentle stream; in this way, five minutes ozonising and five minutes exposure of the plate are quite sufficient to give a dark picture when Ilford special rapid plates are used.

The mode of experimenting may be varied as follows:—A box of lead was taken and a sheet of rubber stretched over the top; this rubber was held in position conveniently by the lid of the box, also of lead. Two tubes of the same metal are provided for the entrance and exit of air, and these tubes have their openings beneath the rubber diaphragm. The tubes are bent so as to render the box light tight (Fig. 1). If now a plate be put into the box with its sensitive film facing the surface of the rubber, and a coin or piece of glass or quartz be placed upon it, no picture is obtained, by passing ordinary air through the apparatus; neither is any picture obtained if ozonised air be used and the rubber be absent. If, however, ozonised air and rubber be used, a picture is easily obtained in a few minutes. The effect is not one of light, since the quartz and glass appear equally opaque to the effect as the metals.

The rubber, on testing, is found to be photographically active either before or after removal from the box. The activity persists for some days afterwards, even when the time during which ozonised air has had access to it has only been a few minutes. The action of ozone on rubber is well known as regards its physical effects. If rubber tubing be used to convey ozonised air, it rapidly becomes so changed that, on slightly stretching it, it breaks up in transverse rings. The action is well shown on photographs

of rubber sheeting obtained by contact in the dark. If the ozonisation has been continued so long as to have caused the rubber to break, the broken edges are beautifully distinct on the photograph. This indicates that the activity of the rubber arises from some product of the action of ozone on the rubber itself, as distinct from any action that may occur between the ozone and the water or other bodies present.

The effect of ozonised rubber is probably due to the formation of hydrogen peroxide. Indiarubber yields on distillation, at moderate temperatures, bodies such as isoprene, more or less allied to the terpenes. Thus it seems possible that rubber itself consists largely of bodies chemically related to the terpenes. The latter are well known to yield hydrogen peroxide on oxidation, and Russell has shown that all the terpenes are photographically active.

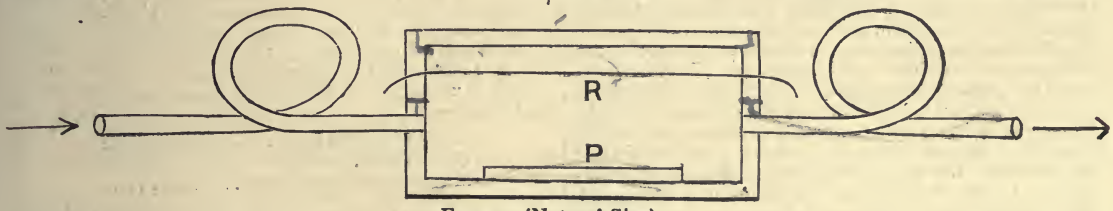


Fig. 1.—(Natural Size).

R, Indiarubber. P, Plate.

Mr. Bryan was good enough to test some rubber sheets in his apparatus for investigating the effect of bodies on the contact difference of potential between two metals. He found that rubber itself had no influence, while ozonised rubber and rubber exposed to the vapour of hydrogen peroxide had an effect in the same sense. This result is not properly to be interpreted by remarking that ozone and hydrogen peroxide both affect the rubber similarly, since hydrogen peroxide apparently has no chemical action on rubber. It rather shows that hydrogen peroxide is a product of ozonisation of rubber.

Transfer Pictures.

If a plate, after being subjected to the influence of the ozonised rubber, be placed upon another plate before development, then, after the films have been in contact some time, the picture may be developed on both the plates. Thus these pictures can not only be taken, but also in a sense printed, in the dark. Prof. J. J. Thomson informs me that Russell has also obtained such pictures; a similar phenomenon is mentioned in Russell's papers, in which the first photographic film is replaced by a non-active body capable of transmitting the effect. This capacity of printing transfers is of use in satisfying the experimenter that any particular effect is not due to radiation of any type. Such transfer pictures have been said to be capable of production by light. But the universal practice of photographers is to store exposed plates film to film before development. No such phenomenon ever occurs as the one exposed plate affecting the other. Another reason for thinking that any such effect is absent is found in the total lack of any accumulative continuing action of light on a photographic dry plate. Experiments to obtain transfers with dry plates and daylight were carried out, both with normal exposures and also with exposures producing solarisation, but not the slightest effect could be obtained. These remarks do not apply to the bichromate processes in which continuing action does occur (Vogel, "The Chemistry of Light and Photography," 1875, p. 242), as is well known, and transfer pictures by contact in the dark can be obtained (*Brit. Journ. Phot. Almanack*, 1899, p. 822).

The active agent from ozonised rubber passes through paper, gelatin, tracing paper, &c., in the same way as with Russell photographs; and bodies like the metals, glass, and quartz are opaque to it.

Sensitiveness of this Test for Ozone.

The amount of ozone necessary to obtain these pictures seems to be very small; for if the positive or negative brush discharge from a small Wimshurst machine be allowed to play on a disc of metal with a central aperture leading through one of the lead tubes to the box in the apparatus above described, the pictures can be obtained in an hour, even without drawing the ozonised air over the rubber. The ozone necessary reaches the rubber by diffusion only.

Tests for H_2O_2.

A glass tube, 2 feet long and an inch wide, was loosely packed with shreds of pure rubber. Ozonised oxygen, after passing through the tube, was photographically active. The rubber was then washed with water, and the latter gave the tests for H_2O_2 with chromic acid and titanic acid. This water was also exceedingly active photographically; a plate placed a quarter of an inch from its surface gave a good picture in ten minutes, while painting the liquid on to the plate produced solarisation almost immediately.

Experiments with other Bodies.

The common varieties of gutta-percha also become fairly active on ozonising; but pure gutta-percha becomes only slightly active, so as to require ozonised air to be in contact with the sheet for a quarter of an hour, and a subsequent exposure of the plate for half an hour, in order to obtain a picture capable of development.

It is interesting to note that camphor also becomes active by treatment with ozone. In experimenting with bodies other than rubber it is best to use oxygen instead of air, as this is an economy of time. On ozonising camphor for ten minutes, it becomes active enough to give a good picture with a quarter of an hour exposure. As Russell has previously shown, camphor, indiarubber, and gutta-percha are ordinarily quite inactive, though capable of transmitting the active agent.

Those other bodies (including cork, vulcanite, and gelatin) which have been tested with ozone are either inactive or else the effect is much less than in the above cases.

Cavendish Laboratory, Cambridge.

SODIUM ALUMINATE AS A MEANS FOR THE REMOVAL OF LIME AND SUSPENDED MATTER FROM WATER FOR USE IN BOILERS.*

By CHARLES F. MABERY and EDWIN B. BALTZLEY.

Throughout the section of country including Northern Pennsylvania, Ohio, and farther west, in districts removed from the lake or the large rivers, the only sources of water in seasons of drought are deep wells. Since the water from these wells contains large quantities of lime

* Contributions from the Chemical Laboratory of the Case School of Applied Science. From the *Journal of the American Chemical Society*, xxi., No 1. (The work described in this paper formed the subject of a thesis for the degree of Bachelor of Science).

salts, there are serious difficulties in the way of procuring water suitable for use in steam boilers, especially in locomotive boilers. Even such water as that from Lake Erie or the rivers, deposit scale to such an extent as to occasion extreme inconvenience. In stationary boilers, the deposition of scale may be avoided at least in part by using some one of the many so-called scale preventatives, if the boiler is in charge of an intelligent engineer.

The inconvenience of boiler scale, the additional cost in fuel, the injury to the boiler, and the danger are features of this question familiar to all who have charge of boilers. The large masses of scale withdrawn from boilers in which hard or turbid water is used, are not surprising when the great quantities of water evaporated in boilers under high pressures are taken into consideration.

The wide variations in the composition of boiler scale are dependent on the differences in the water used. The manner of running the boiler has much to do with the hardness of the scale and the rapidity of its formation. The chief causes of the formation of scale are the calcium carbonate and sulphate and magnesium carbonate contained in solution, and the solid matter held in suspension, both inorganic and organic. All these points must be borne in mind if unpurified water is to be used in a boiler. There has been for some time a feeling on the part of engineers that the only satisfactory method for the prevention of boiler scale is the use of purified water, and many attempts have been made, with more or less success, toward purification of the water before it enters the boiler. The means that have been tried include sedimentation, precipitation by sodium carbonate, sodium hydroxide, slaked lime either alone or in combination. Evidently successful purification depends on removing completely the suspended matter as well as the precipitation of the lime and magnesia. In thinking of what combination should most effectually and economically accomplish these results, in any hard or turbid water, it occurred to one of us (Mabery), that sodium aluminate should fulfil the conditions demanded, and in trying this reagent we find that it meets all requirements.

The general method includes the preparation of sodium aluminate in solution. This may be done in any suitable tank or reservoir, by adding sodium hydroxide in the proper amount to a solution of aluminum sulphate of known strength, and adding to the water a definite amount (the quantity depending on the composition of the water to be purified), agitating thoroughly, and allowing the mixture to stand some time, perhaps twelve to twenty-four hours. The method is based on the following reactions:—

For the formation of sodium aluminate—

$$Al_2(SO_4)_3+8NaOH=Al_2O_4Na_2+3Na_2SO_4+4H_2O.$$

In the precipitation—

$$CaH_2(CO_3)_2+Al_2O_4Na_2+2H_2O=$$
$$=CaCO_3+2AlO_3H_3+Na_2CO_3.$$

$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

Similar reactions evidently take place with magnesium carbonate or sulphate. No doubt sodium aluminate can be made much more cheaply by fusing a tolerably pure clay with soda-ash. Doubtless it may also be obtained cheaply as one of the products in the preparation of soda-ash from cryolite.

Numerous experiments were made with different proportions of sodium aluminate; the best results were obtained by using from one-half the calculated proportions to the calculated proportions of aluminum sulphate, depending on the composition of the water. With proper proportions of aluminate, aluminum hydroxide was completely precipitated on standing. Experiments on different waters with one-fourth the calculated proportion of aluminate showed that this amount was not sufficient to precipitate the lime sufficiently. In applying this method its effect was studied on waters containing different amounts of carbonate and sulphate, as well as on waters with a great variation in turbidity, from the slightly turbid lake water, to specimens thick and muddy. In every instance after standing from twelve to twenty-four hours, the water became perfectly clear. The extent to which lime and magnesia were removed is shown by results obtained in the following waters:—

Very hard water from well in Ohio—

Calcium sulphate	259·0
Calcium carbonate	146·0
Magnesium carbonate	177·3

About 85 per cent of the amount of aluminate required to precipitate all the lime and magnesia was added, air was blown through the solution for a few minutes and the mixture allowed to stand twenty-four hours. Analysis then showed that 88 per cent of the lime had been removed and 95·6 per cent of the magnesia. In another determination the theoretical amount of aluminate was added and the solution treated as before. Analysis showed that 98·1 per cent of the lime had been removed and 97·4 per cent of the magnesia.

The next water tried was the Massillon city water, containing—

Calcium sulphate	99·12
Calcium carbonate	113·2
Magnesium carbonate	131·1

After treatment with the theoretical amount of sodium aluminate the total lime removed was equivalent to 98·8 per cent, and that of magnesia 98·0 per cent.

In another experiment, using one-half the theoretical amount, the lime removed was 83·5 per cent, and that of the magnesia 90·6 per cent.

The next water tried was a very turbid sample from the Cuyahoga river. This water was very muddy and did not settle on long standing. It is used in boilers. A clear sample of this water showed the following composition:—

Calcium sulphate	68·0
Calcium carbonate	14·14
Magnesium carbonate	21·3

Treatment with the theoretical amount of aluminate gave unsatisfactory results.

With twice the theoretical amount, the lime remaining was 88·3 per cent, and the magnesia 84·5 per cent. The aluminate is especially serviceable in such waters as this in removing completely the turbidity.

Although the water of Lake Erie does not contain a large proportion of solid matter, it forms scale quite rapidly unless some means are taken to prevent it. Analysis of a sample collected April 28, 1898, gave—

Calcium carbonate	53 63
Calcium sulphate	32·61
Magnesium carbonate	21·53

Analysis, after treatment with theoretical alnminate, gave 97·6 per cent lime, and 93·2 per cent magnesia removed, after standing thirty-six hours. With one-half the theoretical amount standing forty-eight hours 98·3 per cent of the lime was removed and 90 per cent of the magnesia. With one-fourth the theoretical amount 83 per cent of lime was removed and 60 per cent of the magnesia.

From a very muddy brook water containing much suspended matter, with—

Calcium sulphate	8·1
Calcium carbonate	120·0
Magnesium carbonate	23·0

after standing forty-eight hours, the theoretical amount of aluminate removed 96 per cent of lime and 96 per cent of magnesia. One-half the theoretical amount removed 94·6 per cent lime, and 94·4 per cent magnesia.

In treating the water from a well in Ashtabula, O., containing—

Calcium sulphate	96
Magnesium sulphate	39

the theoretical amount of aluminate removed 98·3 per cent of the lime and 96 per cent of the magnesia.

A well in Glenville, O., containing—

Calcium carbonate	99
Calcium sulphate	36
Magnesium carbonate	23

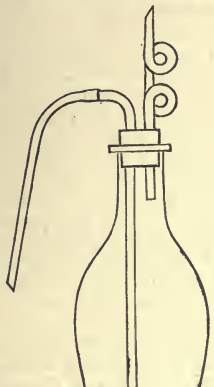
after treatment with theoretical aluminate showed that 98·1 per cent of the lime had been removed and 95 per cent of the magnesia.

To test still further the efficiency of the aluminate, experiments were made with sodium hydroxide alone, using various proportions, but the removal of lime was not much more than half the quantity taken out by aluminate, and the magnesia was not affected. An important effect of alumina is to remove suspended matter, which it does rapidly and completely.

AN APPARATUS TO FACILITATE HYDROGEN SULPHIDE PRECIPITATIONS.*

By RICHARD K. MEADE.

The piece of apparatus described below has been in use here for the past term by the students of my class in qualitative analysis and answers fully the purpose for which it was designed: to hasten the precipitation of the copper-arsenic group by hydrogen sulphide. It consists of an ordinary flask or gas bottle of any suitable form and capacity, provided with a closely-fitting two-hole rubber stopper. A piece of glass tubing bent at right angles passes through one hole to the bottom of the flask, serving as an inlet for the gas. This is connected with the hydrogen sulphide generator by a half or



three quarters of a yard of light rubber tubing. A piece of glass tubing bent in the gas flame to the form shown in the cut passes through the other hole and serves as an outlet for the gas.

The solution to be precipitated is poured into the flask, this in turn corked up, and the apparatus stood in the hood. The gas is now passed into the solution and the flask violently shaken by hand. The bends in the exit tube keep any of the solution from being thrown out of the flask. The churning up of the solution with the hydrogen sulphide gas quickly throws out of solutions the metals of the copper-arsenic group.

The young men tell me that not only is the time necessary for complete precipitation greatly shortened, but the sulphides are obtained in a form more easily filtered and washed, by the use of this apparatus.

* Contributio i from the Chemical Laboratory of Lafayette College. From the *Journal of the American Chemical Society*, xxi : Nc 5.

THE MANUFACTURE OF BARIUM CHLORIDE AND PERMANENT WHITE.

By K. W. JURISCH.

Some time ago, at a chemical works in the North of France, the following operations were carried on:—

Witherite was dissolved in hydrochloric acid and the solution of barium chloride, freed from the greater part of the iron, was evaporated down, or else treated with sulphuric acid, with the object of producing permanent white.

The witherite employed had the following composition:—

$BaCO_3$..	85·98	88·77	77·61
$CaCO_3$..	0·68	2·75	3·91
Fe_2O_3	0·1112	1·17	11·30 (insoluble)
Al_2O_3		7·24	3·58 (insoluble)
SiO_2			1·06
Residue	11·97	—	1·83
Water	0·95	0·25	0·63
	99·6912	100·18	99·92

The crystallised barium chloride contained:—

$BaCl_2$	81·58
$CaCl_2$	1·90
Water	16·22
	99·70

The pasty permanent white as it left the filter-press contained approximately:—

Water	19·75
$BaSO_4$	80·25
$CaSO_4$	Traces

At the present time attempts are being made to replace the witherite—of which the price is high—by heavy spar, which can be obtained at a cheap rate.—*Zeitschrift für Angewandte Chemie*, No. 9, p. 198, 1898.

ON SOME COMPOUNDS OF TITANIC ACID WITH SULPHURIC ACID.

By M. BLONDEL.

I. *Compounds formed with Concentrated Sulphuric Acid.*

Mertz has shown that a solution of titanic acid in sulphuric acid, evaporated rapidly, leaves a gummy mass the composition of which agrees with the formula $TiO_2.SO_3$.

Under slightly different conditions, we have succeeded in preparing two crystalline compounds of titanic acid with sulphuric acid.

The sulphuric solution of titanic acid, heated in a closed vessel, changes in fact at 120° into a mass of crystals having a silky lustre, soluble in water slightly acidulated with hydrochloric acid, having the composition $2TiO_2.3SO_3.3H_2O$.

If we gradually increase the temperature to 225°, the deposit changes into rhombohedric crystals, slowly decomposable by water into basic sulphate and sulphuric acid and having for their composition the formula $TiO_2.SO_3$; under the prolonged action of a temperature

of 225° the whole of the titanic acid leaves the solution and passes into the crystals.

When we attempt to dissolve rutile in concentrated sulphuric acid, and if we allow the temperature to go above 225°, the mineral becomes coated with a layer of sulphate which protects it from complete solution. This will explain the difficulty experienced in dissolving even porphyrised rutile in sulphuric acid. H. Rose recommends diluting the acid with its own volume of water, which diminishes the energy of the acid, but stops the rise of temperature, and consequently the formation of the protective coating. We can with advantage make use of concentrated acid if we carry out the operation in an oven in which the temperature is not allowed to exceed 200°.

II. *Compounds formed in Dilute Sulphuric Acid.*

1. A solution of no matter what proportion of titanic acid in concentrated sulphuric acid, diluted with its own volume of water precipitates, at all temperatures starting from 100°, long needles easily soluble in water, having a composition of $TiO_2.SO_3.2H_2O$.

2. A solution of 0·5 part of titanic acid in 1·0 part of concentrated sulphuric acid, diluted with 1·5 parts of its weight of water, precipitates sulphates of titanic acid of variable composition according to the temperature; at a temperature of 100° the formula will be $2TiO_2.SO_3+Aq.$; at a temperature of 130° the formula is $7TiO_2.2SO_3+Aq.$

3. A solution of any proportion of titanic acid in concentrated sulphuric acid, moderately diluted with water (1 to 5), deposits sulphates up to 175°, and at 175° anhydrous crystallised titanic acid.

4. A solution of any proportion of titanic acid in concentrated sulphuric acid, strongly diluted (1 to 10) with water precipitates at the ordinary temperature, though slowly, the well-defined compound $5TiO_2.SO_3.5H_2O$; at 100° the titanic solution retains, as is well known, traces of sulphuric acid, which cannot be removed even after prolonged washings.

5. Furthermore, a sulphuric solution of titanic acid, first diluted with water and then treated with a small quantity of ammonia, deposits on evaporation *in vacuo* crystals belonging to the cubical system and showing tetrahedric hemihedra. They have for formula $2TiO_2.2SO_3.NH_4O.3H_2O$. These crystals are slowly decomposed by water and effloresce when exposed to the air.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 6.

ON THE CHEMICAL PROPERTIES OF IODOFORM AND ITS DETECTION IN AQUEOUS SOLUTIONS.

By Dr. L. V. STUBENRAUCH.

WHEN we mix a certain quantity of iodoform with a dilute solution of argentic nitrate (at about 1 per cent) at the ordinary temperature no change is observed; but on heating there is a disengagement of carbonic oxide and the formation of a stiff cheese-like precipitate of yellow iodide of silver—

$$CHI_3+3AgNO_3+H_2O=CO+3AgI+3NO_3H.$$

Solid nitrate of silver attacks iodoform in a still more energetic manner and even in the cold. By grinding up these two substances together we notice that heavy fumes of nitric oxide and of iodine are given off, together with the formation of argentic iodide and probably also of carbonic oxide.

We know from Daccomo's work on the subject (*Gazz. Chim. Ital.*, 1871, No. 6, p. 247) that solid iodoform undergoes decomposition under the influence of atmospheric air and of oxygen, while carbonic acid and nitrogen have no action on this body.

Iodoform, when suspended in water, is decomposed by the action of light, the more energetically and rapidly as the intensity of the light is greater. The products of this decomposition are free iodine and hydriodic acid, which both enter into solution, communicating a more or less pronounced yellow colour.

The principal tests which can be used for the detection of iodoform are the following:—

1. The odour, which may, however, be hidden by that of other substances.

2. The microscopic examination of the crystals of iodoform; alcoholic and ethereal solutions give well defined hexagonal tablets. Such an examination may, however, give rise to errors.

3. The action of light, which, as has just been said, decomposes iodoform, colouring its solution yellow. This test is not to be depended upon unless we can be sure of the absence of free hydriodic acid and of alkaline iodides.

4. The phenic reagent of Reiner and Tiemann modified by Lustgarten. We add one or two drops of an alcoholic solution of iodoform to a small quantity of the reagent (20 parts of phenic acid, 40 parts of caustic soda, 70 parts of water) and heat gently. Salicylic aldehyde is formed, and at the same time, owing to a secondary reaction, a red precipitate is formed, which, dissolving in the dilute alcohol, gives it a carmine-red colour. The presence of potassic iodide has no influence, but the experiment does not always succeed.

Fuming nitric acid, used in very small quantity, is an excellent reagent for detecting iodoform in aqueous solutions.

Thus, by adding *one drop* of fuming nitric acid to 3 or 4 c.c. to an aqueous solution of potassic iodide, hydriodic acid or an easily decomposed organic body containing iodine, and then a little starch paste, an intensely blue colouration appears, while iodoform treated in exactly the same manner remains unchanged and does not colour starch. On the other hand, iodoform suspended in water, reduced while hot by powdered zinc and 1 drop of glacial acetic acid, gives a filtrate which gives the blue colour to starch in the presence of fuming nitric acid.

If therefore a solution colours starch blue after having been treated with 1 drop of fuming nitric acid, there is reason to believe that potassic iodide, free hydriodic acid, or a soluble unstable organic compound of iodine is present; but when the acid does not produce iodide of starch, if the blue colour does not show itself until after the reduction by powdered zinc and glacial acetic acid, the presence of iodoform is confirmed.

This reaction is not applicable when the aqueous solution contains besides iodoform, a more or less large proportion of an alkaline iodide, hydriodic acid, or an easily decomposed organic compound of iodine.

The presence of albumen in a moderate amount interferes with the detection of iodoform in aqueous solution by this method.

It is preferable to use a mixture of nitrite of soda and sulphuric acid, instead of fuming nitric acid.—*Zeit. f. Untersuchung der Nahrungs und Genussmittel*, 1898, p. 737.

ON THE DECOMPOSITION OF CARBONIC OXIDE IN THE PRESENCE OF METALLIC OXIDES.

By O. BOUDOUARD.

H. SAINTE-CLAIRE DEVILLE has shown that carbonic oxide dissociates, giving carbonic acid and carbon; he has also established the apparently paradoxical proposition that carbonic oxide, in the presence of red-hot carbon, becomes partially transformed into carbonic acid and carbon (*Comptes Rendus*, vol. lix., p. 873; and vol. lx., p. 317).

Iron, and especially finely divided iron, seems to favour this decomposition. Stammer was the first to notice

(*Ann. de Poggendorff.*, 1851, vol. lxxxi., p. 136), that in passing carbonic oxide over iron, below the softening point of glass, there was besides the iron reduced, a considerable quantity of voluminous carbon uniformly impregnated with iron.

Caron (*Comptes Rendus*, vol. lii., p. 1190) and Lowthian Bell (*Journ. Chem. Soc.*, June, 1869; *Journ. Iron and Steel Inst*, 1871, vol. i., p. 85) have made similar observations, but, contrary to the results of Deville and Gmelin, Lowthian Bell concluded that heat alone does not dissociate carbonic oxide; Deville must have precipitated the carbon of the carbonic oxide at a point where reoxidation was not possible. For this phenomenon to take place, it is necessary to operate in the presence of metallic oxides; the oxides of iron, nickel, and cobalt give the best results.

With the other metallic oxides, operating for longer or shorter periods, at temperatures varying from the melting point of zinc to red-heat Lowthian Bell observed the following facts:—

1. With titanium, the metal appears to be impregnated with carbon.

2. With copper and lead there was no deposit of carbon, but reduction of the oxide to the state of metal.

3. With manganese, no deposit of carbon and reduction to the state of protoxide.

4. With zinc, chromium, tin, and silicon, nothing.

MM. Schlagdenhauffen and Pagel seem to believe, on the contrary, that the deposition of carbon takes place with all the oxides, in particular with oxide of lead (*Comptes Rendus*, vol. cxxviii., p. 311). Now, if we refer to the experiments 387 and 388 of Lowthian Bell, which were made with oxide of lead obtained by the calcination of the nitrate, either at the temperature of fusing zinc, or at a red-heat, we note that no deposit of carbon was observed. The action of carbonic oxide on the oxides of copper and lead, which is so simple since there is only one phenomenon of reduction, is much more complex with the oxides of iron, nickel, and cobalt.

Deville has further noticed that by submitting a bundle of pianoforte-wire placed in a porcelain tube heated for a portion of its length only, so that the middle part is at 1300° and the extremities at 400°, to a current of carbonic oxide, the latter parts only become coated with carbon, the part heated to redness is transformed into steel.

Grüner (*Comptes Rendus*, vol. lxxiii., p. 28; vol. lxxiv., p. 226), has offered the opinion that the ferruginous carbon obtained by the reduction of the oxide of iron by the carbonic oxide always contains a certain proportion of undecomposed oxide of iron, and that pure carbonic oxide cannot deposit carbon on the pure iron. If this is really the fact it should be attributed to the previous presence of carbonic acid in the carbonic oxide, or of sesquioxide of iron in the iron.

According to M. Berthelot, who has studied the action of heat on carbonic oxide (*Ann. Chim. Phys.*, Series 6, vol. xxiv., p. 126; *Comptes Rendus*, vol. cxii., p. 394), the appearance even of carbonic acid in notable quantity, either at a red heat or at 550°, whether with the deposition or not of this element, leaves no doubt as to the mechanism of the decomposition. It is not a simple dissociation; but the decomposition should be preceded by a polymerisation, the condensed product immediately separating into carbonic acid and sub-oxides. The mechanism of this singular transition from this point obeys the same laws as the pyrogenous decompositions and polymerisations of the carbides of hydrogen.

But few experiments have been made from the quantitative point of view. Lowthian Bell has given a large number of determinations relative to the quantities of carbon deposited on known weights of metallic oxides at different temperatures; but he did not estimate the proportions of carbonic acid and of carbonic oxide which were formed.

It occurred to me that it would be interesting to take up this question again; from the theoretical point of view the reaction $2CO=CO_2+C$ comes under the heading of reversible phenomena; from the practical point of view it plays an important part in the working of gas producers. The decomposition of carbonic oxide in fact explains why it is impossible, above all at low temperatures, to obtain this gas without carbonic acid, which is the rule in poor commercial gas. Further, in the metallurgy of iron it would be useful to have numerical data on the decomposition of carbonic oxide in the presence of oxide of iron at different temperatures.

The experiments of Lowthian Bell relative to the decomposition of carbonic oxide in the presence of metallic oxides have shown that the most favourable temperature for the deposition of carbon is 400—450°. According to this *savant*, the difference of importance observed in the deposits of carbon with the different oxides of iron belongs probably to a difference of structure, itself due to the difference of temperature to which the ores have been calcined; further, the phenomenon of the deoxidation of the mineral and that of the deposit of carbon cannot commence at the same temperature. Lowthian Bell therefore thought that the formula for the reaction should be the following:—

$$Fe_xO_y+3CO=3C+Fe_xO_{y+z},\quad x>y.$$

If the action of carbonic oxide on Fe_2O_3 is considered at several intervals we have a mixture of iron, carbon, and an unknown oxide Fe_xO_y, and a series of very complex reactions is produced among the bodies present. According to Lowthian Bell there would, in fact, be a tendency towards the following reactions:—

1. Action of CO on Fe_xO_y, giving CO_2 and a lower oxide of iron.

2. Action of this lower oxide of iron on CO, giving Fe_xO_y and a deposit of carbon.

3. Action of the carbon on Fe_xO_y, giving the metal, the lower oxide, and a mixture of CO and CO_2.

4. Action of metallic iron on CO, giving Fe_xO_y, or the lower oxide, and setting carbon free.

5. Action of CO_2 on the carbon, the metallic iron, and the lower oxide.

There would thus be different equilibria between all the reactions.

I now give the results of researches carried out on oxides of iron, nickel, and cobalt, at a temperature of 445°, which is easy to obtain. I have successively varied the quantities of the metallic oxides in the reaction, and the duration of contact between the metallic oxide and the carbonic oxide.

The carbonic oxide is obtained by the action of sulphuric acid on formate of soda; the gas produced containing 95 to 97 per cent of pure carbonic oxide is collected in Regnault gas-holders. Before entering into reaction it traverses a copper tube 25 c.m. in length, heated to redness, a flask of potash, and a U-tube containing fragments of potash. A control tube containing baryta water shows that the carbonic oxide is completely deprived of carbonic acid before reaching the sulphuric acid drying tubes.

The metallic oxides are used in a very finely divided state, pumice being used to give support (this pumice soaked with the nitrate is calcined at a red heat); they are contained in glass tubes of 15 m.m. internal diameter and 60 to 70 m.m. in length, drawn down to a point at each end. These tubes are placed in communication with the carbonic oxide. When the metallic oxides are completely reduced and there is a deposit of carbon (the gas should be passed for about an hour to effect this), the tube is closed and then heated for some time. At the end of the experiment the tube is taken from the sulphur bath, and the gases extracted by means of a mercury pump and analysed.

The gas must be very carefully extracted while the tube is still warm; there is, in fact, a risk of the formation of metallic compounds with carbon, which the oxide might possibly furnish (sub-carbonate of iron, nickel, and prob-

TABLE I.

Quantities of metallic oxides.	Eight mins.		Forty mins.		Sixty-four mins.		Eighty mins		Three hours.		Six hours.		Seven hours.	
	CO_2.	CO.	CO_2.	CO.	CO_2.	CO.	CO_2	CO.	CO_2.	CO.	CO_2.	CO.	CO_2.	CO.
Oxide of iron 0·0673 grm. ..	30·2	69·8	57·4	42·6	—	—	87·0	13·0	94·8	5·2	100	—	—	—
,, 0·224 ,, ..	16·1	83·9	—	—	62·9	37·1	—	—	—	—	—	—	100	—
,, 0·222 ,, ..	2·9	97·1	—	—	36·6	63·4	—	—	—	—	52·3	47·7	—	—

TABLE II.

Quantities of of metallic oxides.	Eight minutes.		Sixty minutes.		Two hours.		Four hrs. 15 mins.	
	CO_2.	CO.	CO_2.	CO.	CO_2.	CO_2.	CO_2.	CO.
Oxide of nickel 0·15 grm. ..	100	—	—	—	—	—	—	—
,, 0·05 ,, ..	90·9	9·1	100	—	—	—	—	—
,, 0·005 ,, ..	25·9	74·1	88·4	11·6	96·3	3·7	100	—
Oxide of cobalt 0·15 grm. ..	100	—	—	—	—	—	—	—
,, 0·05 ,, ..	89·7	10·3	100	—	—	—	—	—
,, 0·005 ,, ..	47·6	52·4	81·2	18·8	93·9	6·1	100	—

ably cobalt). I noticed this fact with some tubes containing oxide of nickel which had been closed in August, 1898, and were opened in the following October. The pieces of pumice contained in the tube, on being heated, gave rise to the formation of a metallic film, due to the decomposition of the sub-carbonate of nickel formed on cooling. The most favourable temperature for the formation of sub-carbonate of nickel is about 50°.

I. The experiments were carried out on quantities of metallic oxides varying in the proportion of 30 to 1; the time of heating varied from eight minutes to seven hours. The results obtained were as follows. (See Tables I. and II.).

These figures indicate the quantities per 100 of carbonic acid formed and of undecomposed carbonic oxide. Together these results show that the reaction of the decomposition of the carbonic oxide is a function of time, and that it also depends on the quantity of metallic oxide present. With the oxides of nickel and cobalt a much longer time is required than with oxide of iron to arrive at complete decomposition. In the third set of experiments, made with oxide of iron, after six hours heating the decomposition was not complete; but there is no doubt that after the lapse of a sufficiently long time a result would be obtained identical with the others.

II. In the above-mentioned experiments, both with the oxide of iron and the oxides of nickel and cobalt, the quantities of carbon deposited at the moment of closing the tubes was in the same proportion as the quantities of metallic oxides present. In a second series of experiments, I took wood-charcoal, calcined in a current of chlorine to remove what hydrogen it might contain; this carbon, in fragments about the size of a nut, was impregnated with a solution of nitrate of iron, nickel, or cobalt, and calcined. I then had to do with large quantities of carbon relative to the quantities of oxide present; with iron the proportion of carbon was 13 : 1; with nickel and cobalt, 9 : 1. The experiments were carried out in the same manner as the preceding ones and at the same temperature, viz., 445°. The results were as follows:—

TABLE III.

Quantities of metallic oxides.	Eight minutes.		Six hours.	
	CO_2.	CO.	CO_2.	CO.
Oxide of iron 0·244 grm. ..	33·3	66·7	84·1	15·9
,, 0·008 ,, ..	7·9	92·1	79·7	20·3
	Eight minutes.		Four hours fifteen mins.	
Oxide of nickel 0·244 grm. ..	64·0	36·0	99·1	0·9
,, 0·0158 ,, ..	25·3	92·1	65·4	34·6
Oxide of cobalt 0·417 ,, ..	96·4	3·6	98·8	1·2
,, 0·0139 ,, ..	17·4	82·6	84·4	15·6

The progress of the reaction is thus the same; we get a total decomposition of carbonic oxide by sufficiently prolonging the heating. With the oxides of nickel and cobalt a shorter time is required than with oxide of iron to arrive at the same results. We would, however, remark in a general way that there is a slowing down of the phenomenon; and that, other things being equal, in this second series of experiments the decomposition of the carbonic oxide is effected much more slowly.—*Bull. Soc. Chim.*, Series 3, xxi., No. 6.

SOME PROPERTIES OF LIQUID AMMONIA.

By E. C. FRANKLIN and C. A. KRAUS.

THE authors have been led to undertake the study of the properties of liquid ammonia in considerable detail with the object of following out, to as great an extent as possible, the manifest close relation which exists between this solvent and water. Although it has long been recognised that many derivatives of water have their analogues in certain ammonia derivatives, still the intimate relation existing between the two liquids seems never to have been fully recognised.

Water occupies an essentially unique position among the well-known solvents. Its physical properties, such as its capacity as a general solvent for salts and its power of electrolytic dissociation, its low molecular elevation constant, its high boiling-point, and its heat of fusion, heat of volatilisation, critical temperature and critical pressure, specific heat, association constant and dielectric constant, with values so very much higher than the corresponding values for other substances, all tend to remove it far from other solvents, and to place it in a class by itself.

From the considerations submitted below it will be recognised that, of all known liquids, ammonia most closely approaches water in all those properties which give to water its conspicuous position among solvents. In its capacity as a general solvent for salts it is secondary to water, but superior to all other solvents. It closely approaches water in its power of dissociating electrolytes; some salts conduct electricity even better in ammonia solution than they do in aqueous solution. It plays a part in many compounds analogous to that occupied by water in salts containing water of crystallisation. Its heat of volatilisation and probably its association constant are higher than those of any other liquid with the one exception of water. For a substance of such simple composition its critical temperature and critical pressure, and even its boiling-point at atmospheric pressure, are remarkably high, as is still more conspicuously true of the corresponding constants in the case of water. Its specific heat is quite as great as that of water, while its molecular elevation constant is lower than that of any other substance for which measurements have yet been made.

Ammonia differs from water in its inability to dissolve the sulphates and sulphites, the alkaline carbonates, phosphates, and oxalates, the hydroxides of the alkali and alkaline earth metals, and the facility with which it dissolves many organic substances, in which latter respect it reminds one of alcohol rather than of water. The liquid does not exhibit a maximum density (Faraday, "Watts's Dictionary," 2nd Ed., vol. i., p. 183) above the freezing-point, nor is the solid ammonia specifically lighter than the liquid at its freezing-point, as is true of solid and liquid water.

Electrolytic Conductivity of Ammonia Solutions.—Bleekerode (*Phil. Mag.*, 1878, [5], v., 384, and *Wied. Ann.*, 1878, iii., 161), in a paper published in 1878, on the conductivities of the liquefied halogen acids, ammonia, and certain other compounds, makes the statement that liquid ammonia is a good conductor of electricity. There can be no question, however, that he misinterpreted his results. The conductivity he measured was undoubtedly due to a salt of sodium in solution. The passage of the current decomposed the salt, setting free metallic sodium, which, dissolving in the ammonia, gave to the solution the characteristic blue colour.

Divers, in 1873, observed that the concentrated solution of ammonium nitrate in liquid ammonia, formed by the deliquescence of the salt in an atmosphere of ammonia gas, is a good electrolytic conductor (*Proc. Roy. Soc.*, 1873, xxi., 109.

Led to the subject by the study of the similarity of properties, and of constitution of the compounds of salts with water of crystallisation to those compounds in which ammonia plays an analogous part, Cady (*Jour. Phys. Chem.*, 1897, i., 707) discovered that solutions of certain salts in liquid ammonia are conductors of electricity. He measured the conductivity of thirteen salts at moderate concentration, and found that they conduct electricity in ammonia solution at −38°, almost, if not quite, as well as they do in water solution at 18°. He also found that solutions of the alkali metals conduct electricity, and with much greater facility than do salt solutions. Moreover, he pointed out that these metallic solutions show no signs of polarisation at the electrodes.

The authors have extended the list of determinations of the conductivity of metallic salts, and have also made measurements of the conductivity of certain organic compounds, especially the aromatic nitro-compounds, which show themselves to be good conductors in solution in ammonia. The authors have also made measurements of the increase of molecular conductivity with dilution for a number of salts, and have, further, determined the conductivity of a number of solutions at temperatures varying from −79° up to and past the critical temperature of ammonia. The results of this work will be published in the near future.

Metathetic Reactions in Ammonia Solutions.—As in the case of aqueous solutions, electrical conductivity and facility of chemical reaction between substances in solution go hand in hand, so, because of the undoubtedly dissociated condition of salts dissolved in liquid ammonia, precipitates ought to be formed instantaneously when solutions containing ions which are capable of forming salts insoluble in ammonia are brought together. That ammonia solutions do exhibit such behaviour is shown by the results given in the preceding paper on "Metathetic Reactions between Certain Salts in Solution in Liquid Ammonia."

Ammonia of Crystallisation and Ammonia of Constitution.—The authors have up to the present added but one compound to the long list of substances formed by the direct addition of ammonia to many of the metallic salts. Leaving out of consideration at the present time the very great number of such compounds, it will be sufficient to mention the early observations of Divers (*loc. cit.*), who considers the ammonia in the liquid formed by the action of ammonia on ammonium nitrate to be entirely analogous in function to the water absorbed, for instance, by calcium chloride; to the ammonia addition-products described by Joannis (*Compt. Rend.*, 1891, cxii., 337), Jarry (*Ibid.*, 1897, cxxiv., 288 and 963; 1898, cxxvi., 1138), Bonnefoi (*Ibid.*, 1897, cxxiv., 771), formed by the action of liquid ammonia on the salts, and to the slaking phenomena attendant upon the action of liquid ammonia on certain halogen salts first described by Gore (*Proc. Roy. Soc.*, 1872, xx., 441), and also observed by the authors in their investigations on liquid ammonia as a solvent (*Amer. Chem. Journ.*, xx., 820).

Specific Heat of Ammonia.—The specific heat of liquid ammonia has been calculated from thermodynamic data by Zeuner, Ledoux, and Wood. It has also been made the subject of experimental investigation by Regnault, Von Strombeck (*Journ. Frank. Inst.*, 1890, cxxx., 467), Lüdeking and Starr (*Am. J. Sci.*, 1893, [3], xlv., 200), and Elleau and Ennis (*Journ. Frank. Inst.*, 1898, cxlv., 189). For the experimentally determined values, Von Strombeck found 1·22876 at 45°, Lüdeking and Starr 0·8857 at 40°, and Elleau and Ennis 1·021 at 10°. Calculated from Professor Wood's formulæ ("Thermodynamics," p. 325; *Trans. A. I. M. E.*, xii., 136, and x., 645.

*Boiling-point of Ammonia.**—While the boiling-point of ammonia is much below that of water, still it is high when compared with the boiling-points of other simple compounds of elements with low atomic weights. The boiling-points of hydrogen sulphide, hydrogen selenide, the halogen acids, methane, ethylene, acetylene, phosphine, and even arsine, stibine, and hydrogen telluride, are all below, and some of them far below, the boiling-point of ammonia. As is the boiling-point of water, so is the boiling-point of ammonia—although to a less extent—abnormally high.

Heat of Fusion.—No determinations of the heat of fusion of solid ammonia have yet been made.

Heat of Volatilisation of Ammonia.—With the exception of some preliminary measurements by the authors, no direct determinations of the heat of volatilisation of ammonia at its boiling-point at atmospheric pressure have yet been made. Regnault's value (Landolt and Börnstein, "Physikalisch-chemische Tabellen") of 294·21 is the result of measurements made at 7·8°. Von Strombeck (*loc. cit.*, p. 472) obtained 292·4 as the result of measurements made at 14° to 18°. As preliminary results the authors have obtained 326 to 332 as the heat of volatilisation of ammonia at its boiling-point. A description of the method by which these measurements were made, together with the final values, will be published in a later paper.

The heat of volatilisation of ammonia at any required temperature may also be calculated from thermodynamic formulæ. From a formula used by engineers in calculating the capacities of refrigerating-plants, $h_e = 300 - 0{\cdot}8t$ (Peabody, "Thermodynamics," p. 459), the value for the heat of volatilisation of ammonia at −38° is calculated to be 330 calories.

Another formula given by Professor Wood ("Thermodynamics," p. 332), $h_e = 555{\cdot}5 - 0{\cdot}613T - 0{\cdot}000219T$, in which English heat units and Fahrenheit temperatures are to be understood, if used for calculating the heat of volatilisation of ammonia, gives a value of 321 cals. at −38° C.

The heat of volatilisation of a liquid may also be calculated by means of the law of Trouton (*Phil. Mag.*, 1888, [5], xviii., 54), according to which the molecular heats of volatilisation of closely related substances are directly proportional to their absolute boiling-points. In the expression for Trouton's law $\lambda M/T = k$, in which λ is the heat of volatilisation, M the molecular weight, and T the absolute boiling-point, the values of k, in the case of water, methyl alcohol, ethyl alcohol, and amyl alcohol

* Regnault gives 38·5°; Loir and Drion 35·7°; and Bunsen 33·7° as the boiling-point of ammonia. "Watts's Dict. Chem." 2nd Ed., vol. i., p. 183; "Supplement," vol. vi., p. 102. Joannis gives the boiling-point at 38·2°, *Compt. Rend.*, 1893, cxv., 820.

are respectively 25·9, 25·7, 26·3, and 26·2. If we are justified in assuming that ammonia is closely related to water, then by substituting the values, $k=25·9$, $T=235$, and $M=17$, in the formula $\lambda=kT/M$, the latent heat of volatilisation of ammonia is calculated to be 358 cals.

These values, while not in as good accord as might be wished, still agree in showing that the heat of volatilisation of liquid ammonia, of all known liquids, is second only to water.

Molecular Elevation Constant of Ammonia.,— Other than by direct experimental determination, the molecular elevation constant of a liquid may be calculated by means of the formula of van 't Hoff, provided the heat of volatilisation and the boiling-point of the liquid are known. Several approximate values for the heat of volatilisation of ammonia are given above, which by substitution in the formula, $k=0·02T^2/\lambda$, yield the values given below for the molecular elevation. Values for the molecular elevation of the boiling-point, experimentally determined for a number of substances (*Amer. Chem. Journ.*, xx., 836) are also included in the table.

	he.	*k.*
Peabody's formula ..	329	3·35
Wood's ,, ..	321	3·44
Trouton's ,, ..	358	3·09
He direct	329	3·36
Water		3·4
Ethyl alcohol.. ..		3·4
Propyl ,, ...		3·4 to 2·7
Pyridine		3·3 to 1·8
Aniline		3·9 to 3·1
Potassium iodide ..		3·2 to 5·9

Certainly the molecular elevation of the boiling-point of ammonia is smaller than that of any other solvent for which measurements have yet been made.

The Dielectric Constant of Ammonia.—This constant has recently been measured by Dr. H. M. Goodwin (a paper read before Sec. B, American Association for the Advancement of Science, 1898), of the Massachusetts Institute of Technology, who finds a value of about 20. These measurements, if Nernst's hypothesis holds true, show that the dissociation of salts in liquid ammonia may not be as great as we had supposed.

Molecular Association of Ammonia.—Some indication of the degree of association of a liquid may be arrived at by the application of the methods given by J. Traube in a recent paper (*Ber. d. Chem. Ges.*, 1897, xxx., 265).

For liquid ammonia we have calculated the values, 190_{-88}, 23·9, and 0·00079, for—

$$x_2\frac{M\lambda}{T} \text{ and } \frac{MT'-T}{m\ \dot{p}T}$$

espectively (*loc. cit.*, p. 273), results which place liquid ammonia among the associated liquids along with water and the alcohols.

If 55·90, the approximate molecular heat of volatilisation of ammonia, be substituted in place of an incorrect value used in a table recently published by Vaubel (*Jour. Prakt. Chem.*, 1898, [5], lvii., 351), then the association constant of liquid ammonia approaches that of water and excels that of the alcohols instead of indicating ammonia to be a non-associated liquid.—*American Chemical Journal*, xxi., No. 1.

Some Derivatives of Disymmetric Tetramethyldiamidodiphenylethane. — A. Trillat. — The base obtained by condensing acetic aldehyde with dimethylamine shows a close analogy to the derived base of methane. It differs from it, however, essentially in one particular, that it is unable to form colouring-matters. —*Comptes Rendus*, No. 23, June 5, 1899.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 23rd, 1899.

Mr. T. H Blakesley, Vice-President, in the Chair.

A paper "*On the Magnetic Hysteresis of Cobalt*," by Prof. Fleming, Mr. A. W. Ashton, and Mr. H. J. Tomlinson, was read by Mr. Ashton.

A rectangular sectioned circular ring of cobalt was insulated with silk tape, and wound over with four secondary coils put on at quadrantal positions. Over these secondary coils six primary coils were placed, and the ring was submitted to a complete set of magnetic tests with a ballistic galvanometer.

From these observations various curves have been plotted, and the results have been compared with a similar set of readings taken on a cast-iron ring. A chemical analysis of the cobalt showed that it contained about 1 per cent of iron and 1 per cent of nickel. The authors conclude that, although in general form the magnetisation curve for cobalt resembles that of cast-iron, its hysteresis exponent is similar to that of annealed soft iron. The absolute hysteresis values corresponding to various maximum flux densities are, however, not very different from those of a typical variety of cast-iron.

Prof. Everett referred to the fact that the sample of cobalt contained about 1 per cent of iron, and said that it would be interesting to know how cobalt free from iron would behave.

The Chairman said that the hysteresis curves obtained from the step by step method could not be applied to dynamos, because the time taken to perform the cycle altered the shape of the curve. He would like to see the curves for cobalt determined in cases where the cycles were quickly executed.

A "Discussion on Physical Tables" was commenced by Mr. J. Lupton.

Mr. Lupton briefly reviewed some of the difficulties met with in compiling Physical Tables and in keeping them up to date. He divided them into four classes according to their objects, and criticised several well-known books of constants. He pointed out the danger of leaving out apparently obvious figures, and referred to the necessity for accurate proof reading.

Prof. Everett said that, in his work, he had aimed at giving an idea of the meanings of various numbers rather than stating them with great accuracy. He drew attention to the difficulty of condensing large series of numbers into a clear and concise table.

Mr. Watson said that it was important that the units in which numbers were expressed should be stated at the head of each table.

The Chairman having pointed out one or two small points to be attended to in the compilation of tables, the Society adjourned until next October.

Electrolytic Estimation of Cadmium.—E. Rimbach. —The best means for effecting this separation is to use about 150 to 200 c.c. of the dilute solution, add an excess of pure cyanide of potassium, and electrolyse with a current of 0·02 to 0·04 ampère and 3·0 to 3·3 volts. The electrolysis must be kept up for twelve hours, after which the cathode is washed, dried, and weighed. This method is especially suitable for the analysis of alloys containing aluminium, cadmium, and tin, with small quantities of copper. The alloy is dissolved in nitric acid, evaporated in the presence of an excess of hydrochloric acid, and the solution of chlorides electrolysed. By this process we are also enabled to separate cadmium from magnesium, if this latter metal is not present in too great proportion. In such a case an excess of chloride of ammonium must be added to the electrolyte to prevent the precipitation of the magnesium.—*Zeit. Anal. Chem.*, xxxvii., [5], p. 284.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 22, May 29, 1899.

Estimation of Hydrogen Phosphide in Gaseous Mixtures.—A. Joannis.—The author's experiments show that sulphate of copper can only be employed to estimate phosphoretted hydrogen contained in gaseous mixtures in the absence of gases which are absorbed by copper salts. In the latter case, only a quantity of copper sulphate sufficient for the reaction must be used—two molecules of sulphate to one of phosphide. For example, 1 c.c. of the saturated solution for 10 c.c. of the gas.

Separation and Estimation of Traces of Chlorine in presence of a very Large Excess of Bromine.—A. Baubigny.—In several recent papers, a method of estimating small traces of chlorine by the action of bromine on chlorides has been described. The author's researches show that in dilute solution, relatively poor in chlorides, the salts appear to undergo no alteration, in spite of the presence of a large excess of free bromine. By his modification of this method minute traces of chlorine are able to be detected in bromides.

Properties of some Mixed Halogen Salts of Lead.—V. Thomas.—By dissolving lead iodide in a saturated hot solution of lead bromide, greenish yellow needles of bromiodide are deposited; the first crop having the formula $3PbBr_2PbI_2$. Analysis of the resulting product shows gradually less and less of the iodide. At a low temperature the crystals are formed of pure lead bromide. If, instead of separating the first crops of crystals by filtration, they are left to cool in the solution, the whole is transformed into bromiodide. On heating the solution the crystals dissolve and decompose. These results can be easily explained if the fact of the dissociation of the mixed salts is admitted.

Quantitative Separation of Cerium.—G. Wyrouboff and A. Verneuil.—The great difficulty of separating quantitatively any single one of the rare earth group is due to two properties common to these earths: their polymerisation and their faculty for forming exceedingly stable compounds among themselves. To estimate the cerium present in presence of other rare earths, the nitric acid solution of their oxides is precipitated by ammonia and peroxide of hydrogen. This is evaporated on a water-bath and heated for a few moments until the NH_4NO_3 begins to volatilise. The whole is then dissolved again in HNO_3 and evaporated to a syrupy state, but not further, dissolved in boiling water, and a slight quantity of $(NH_4)_2SO_4$ added. The precipitate formed is filtered, washed, and heated to a white heat. If the operation has been successful, the product should contain 90 per cent of the total cerium in a perfectly pure state. The filtrate is then added to 0·05 gr. of ammonium persulphate and 1 c.c. of 50 per cent acetate of soda solution. The whole is boiled until the liquid becomes clear and well separated from the precipitate, which latter is filtered, washed, and strongly heated. This precipitate should consist of the remainder of the cerium of a pale yellow colour.

Mixed Compounds of Phenylhydrazine and another Organic Base with Metallic Salts.—J. Moitessier.—Certain combinations of metallic salts with phenylhydrazine can be made to unite with further molecules of this base, giving compounds very rich in phenylhydrazine. In the same manner they can be made to unite with other organic bases (aniline, naphthylamine, &c.), giving mixed compounds. These latter compounds can be also prepared by the simultaneous action of phenylhydrazine and another organic base on the metallic salts. The author prepared the following compounds by this method:—

Aniline phenylhydrazinic iodide of zinc,—

$$ZnI_2.C_6H_5.NH_2.2C_6H_5.N_2H_3;$$

aniline phenylhydrazinic bromide of zinc,—

$$3ZnBr_2.5C_6H_5.NH_2.2C_6H_5.N_2H_3;$$

aniline phenylhydrazinic sulphate of nickel,—

$$NiSO_4.C_6H_5.NH_2.2C_6H_5.N_2H_3+2H_2O;$$

aniline phenylhydrazinic nitrate of cadmium,—

$$2N_2O_6Cd.3C_6H_5.NH_2.5C_6H_5.N_2H_3;$$

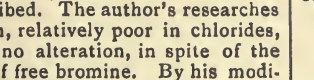
α-naphthylamine phenylhydrazinic iodide of zinc,—

$$ZnI_2.C_{10}H_7NH_2.2C_6H_5.N_2H_3;$$

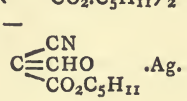
β-naphthylamine phenylhydrazinic iodide of zinc,—

$$3ZnI_2.2C_{10}H_7.NH_2.4C_6H_5.N_2H_3.$$

Oxymethylenic Derivatives of Cyanacetic Ether.—E. Grégoire de Bollemont.—The author has prepared a series of compounds from the sodium salt, which is prepared by the action of amyl formate on dry cyanacetic ether at 100°. From this are prepared the barium salt,—



and the silver salt,—



Bulletin de la Société Chimique de Paris. Series 3, Vol. xxi., No. 3.

Action of Bibromide of Acetylene on Pyrocatechin in the presence of Alkalis.—Ch. Moureu.—One molecule of bi-bromide of acetylene, one molecule of pyrocatechin, and two molecules of alkali are added together. A reaction takes place, but not the one expected; there is no action in the cold, but it occurs with violence—and sometimes with explosive force—under the influence of heat. Whether the alkali is in aqueous or alcoholic solution, dilute or concentrated, bromised acetylene gas, $CH{\equiv}CBr$, is formed rapidly by heating; this gas ignites spontaneously in the air with the production of a thick smoke. Di-soda or di-potash pyrocatechin reacts on bromide of acetylene, with the elimination of hydrobromic acid, in the same manner as with free alkali, and ethenic pyrocatechin is not formed.

Glyoxal Dipyrocatechin.—Ch. Moureu.—One molecule of tetrabromide of acetylene was gradually added to a mixture of two molecules of pyrocatechin, four molecules of potash, and water equal to about one quarter the weight of the potash. This was shaken continuously and kept at a temperature of about 60°. The reaction is very lively, and gas is given off abundantly. Finally, the whole is heated in a flask fitted with a vertical condenser in an oil-bath for four hours. The cooled mass is then treated with an excess of potash or soda-lye and submitted to the action of a current of steam. The various phenolic compounds remain in the alkaline solution and a neutral oily substance is gradually carried over, and condenses in the form of white masses completely insoluble in water. The product crystallises in alcohol in thin light leaflets, melting at 88—89° and having the formula $C_{14}H_{10}O_4$. This new compound appears to be a normal regular condensation product of glyoxal and of pyrocatechin, for which we propose the name glyoxal-dipyrocatechin. After heating this new body with dilute sulphuric acid for four hours in the same flask, pyrocatechin is found in the water of hydrolysis, but no glyoxal. It is also shown, however surprising it may be, that glyoxal-dipyrocatechin, glyoxalic diacetal of pyro-

catechin, and consequently the aldehydic derivatives, furnish by simple hydratation a compound at the same time acid and phenolic, viz., orthoxyphenoxyacetic acid.

On Glyoxal-monopyrocatechin Aldehyde.—Ch. Moureu.—According to the preceding paper, glyoxal-monopyrocatechin aldehyde, $C_6H_4<^{(1)\,O}_{(2)\,O}>CH-CHO$, should necessarily constitute the first intermediate product of the hydrolysis of glyoxal-dipyrocatechin, $C_6H_4<^{O\ (1)}_{O\ (2)}>CH-CH<^{O\ (1)}_{O\ (2)}>C_6H_4$. From this it follows that this aldehyde, when hydrolysed directly, should produce orthoxyphenoxyacetic acid, as does glyoxal-dipyrocatechin itself. The author then goes on to show that such is really the case.

On Orthoxyphenoxyacetic Acid, and on Phene-orthodioxyacetic Acid.—Ch. Moureu.—This note sums up a certain number of facts which have been observed in the course of the work described in the two previous papers, but which are not in immediate relation with this work. (1) Orthoxyphenoxyacetic acid is not a phenolic acid properly speaking, the carboxyl not being directly linked to the aromatic nucleus; the substance is in reality a substituted acetic acid. Its ethylic ether is easily obtained by heating with a reflux condenser equal molecules of monochloracetate of ethyl and mono-soda pyrocatechin in alcoholic solution. (2) At the same time as the above acid is formed, there is also another one arising from the condensation of monochloroacetic acid with pyrocatechin. The mother-liquors from this preparation slowly deposit a white powder, forming, after crystallisation, fine needles melting at 172—174°. This compound is phene-orthodioxyacetic acid, $C_6H_4<^{O-CH_2-CO_2H\ (1)}_{O-CH_2-CO_2H\ (2)}$.

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Persons desiring to submit Tenders may obtain the Specifications, Forms of Tender, and other particulars at the Engineer's Department, County Hall, Spring Gardens, S.W. Tenders must be upon the official forms, and the printed instructions contained therein must be strictly complied with. The contractors will be required to pay to all workmen employed by them such wages and to observe such hours of labour as are generally accepted as fair in the trade. Tenders are to be delivered at the County Hall in a sealed cover addressed to the Clerk of the London County Council, and marked "Tender for Lime or Proto-sulphate of Iron" (as the case may be). No Tender will be received after 10 a.m. on Tuesday, the 11th July, 1899. Any Tender which does not comply with the printed instructions for tender may be rejected.

The Council does not bind itself to accept the lowest or any Tender, and it will not accept the Tender of any person or firm who shall on any previous occasion have withdrawn a Tender after the same has been opened unless the reasons for the withdrawal were satisfactory to the Council.

C. J. STEWART,
Clerk of the Council.
Spring Gardens, S.W.,
24th June, 1899.

TO MANUFACTURING CHEMISTS and OTHERS.

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C. J. STEWART,
Clerk of the Council.
Spring Gardens, S.W.,
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THE

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No. 2067.—JULY 7, 1899.

THE CLASSIFICATION OF CHEMISTRY,

As Proposed by the Committee on the International Catalogue of Scientific Literature.*

A Critical Analysis.

By H. CARRINGTON BOLTON
and
WILLIAM P. CUTLER.

If the object of arranging titles of books in a bibliography in certain groups or classes is to enable readers and investigators to find more readily an article on a given subject, then the *anonymous* Committee that drew up the schedule of classification for Chemistry in the Report of the Royal Society's International Catalogue Committee has made an almost total failure.

Two methods were open to the Committee appointed to devise a classification scheme for Chemistry, either to adopt an arbitrary system, in which symbols uniformly indicate definite subjects, or to adopt the dictionary plan, in which specific words are arranged alphabetically. The latter plan has, in our opinion, great and incontestable advantages over the former, but as the Committee chose to adopt the first named method the second cannot be here considered.

The provisional plan which was submitted to the delegates at the Conference of the International Catalogue Committee, held in London, October, 1898, forms Section F, of the general scheme printed in a small volume, very difficult for others than delegates to obtain. The grand divisions, with their registration symbols, are as follows:—

(No number) Chemical Bibliography.
0100 Chemistry (Specific) of the Elements.
0900 Laboratory Procedure.
1000 Organic (Carbon) Chemistry (Specific).
1010 Hydrocarbons.
1100 Alcohols and Ethers.
1200 Acids.
1300 Aldehydes and Ketones.
1400 Carbohydrates; Glucosides; Resins.
1500 Amino- and Azo-Compounds.
1600 Mixed Cycloids.
1700 Organo-Metallic and Allied Compounds.
1800 Alkaloids.
1900 Proteids.
2000 Coloured Compounds.
2500 Operations in Organic Chemistry.
3000 Analytical Chemistry.
3500 Theoretical and Physical Chemistry.
4000 Physiological Chemistry.

These grand divisions are sub-divided so as to provide a class and a symbol for every substance known to the chemist or awaiting discovery; at least such is the intention. Chemical Bibliography is divided into six groups, to wit:—

0000 Philosophy.
0010 History.
0020 Biography.
0030 Dictionaries, collected works, monographs, and text-books.
0040 Pedagogy.
0050 Addresses, lectures, essays, and theses.

Curiously, no symbol is provided for bibliographies of chemistry, a topic that must have been prominent in the minds of the persons on the Committee.

The second grand division "0100 Chemistry of the Elements" is intended to embrace "all specifically chemical subject-matter, and such other entries as may be desirable, relating to the elements generally, excepting carbon." In this catagory the elements are arranged alphabetically, and to each a symbol is given, thus:—

0110 (Al) Aluminium.
0120 (Sb) Antimony.
0130 (A) Argon.
* * *
0200 (Cd) Cadmium,
0210 (Cs) Cæsium.
* * *

* Advance proofs from *Science*, June, 1899.

0250 (Cl) Chlorine.
0260 (Cr) Chromium.
* * *
0800 (Va) Vanadium.
0810 (Yt) Ytterbium.
0820 (Y) Yttrium.
0830 (Zn) Zinc.
0840 (Zr) Zirconium.

Students, and even older chemists, who find difficulty in recalling the atomic weights of common elements, will scarcely welcome the proposition to give to each element another factor, though in the case of antimony this objection disappears.

This alphabetical arrangement of the elements prevents carrying out one of the prime objects of classification, namely, the grouping of related matters; thus—

0270 = Cobalt, 0500 = Nickel,
0690 = Sulphur, 0710 = Tellurium.

The natural group Ba, Ca, and Sr have respectively the unrelated numbers 0150, 0220, and 0680. Surely the elements might have been arranged systematically, so that related bodies would have contiguous symbols.

Annexed to the table of elements are instructions for sub-dividing entries and the following paragraph:—"Specific entries relating to the halogens collectively shall be arranged in Division 0250 under *Halogens*." This mixing of a word-heading with numerical symbols is a weak feature to be again noticed.

The instructions for entering titles in sub-divisions of 0100 include the following paragraph:—"Entries relating to compounds, which in the Slip Catalogue bear the number and symbol of the dominant element, together with the symbol of the secondary constituent, or dominant second constituent, shall be printed in the sub-division of their second constituent." If we understand aright this rather obscure sentence, it provides for writing on slips according to one rule and for printing them in book form according to another rule; sodium chloride would appear, therefore, under the symbol for sodium in the written slips and under chlorine in the printed volume!

A second paragraph provides that "references to hydroxides, acids, and salts shall be entered under the oxide, and corresponding sulphur compounds under the sulphide."

A third paragraph reads as follows:—"(*d*) In each sub-division the entries shall be arranged in such order that those relating, α, to the history or origin of the substance come first, and following these, in the order mentioned, those relating, β, to its preparation or manufacture; γ, to its structure, or of a theoretical nature; δ, to its interactions or use; ϵ, to its compounds—these five several sections being denoted by the letters α, β, γ, δ, ϵ."

Passing without comment this non-parsable English (which occurs elsewhere in the report), the scheme introduces another arbitrary feature, Greek letters for specific subjects, which is an admission that the numerical plan is found insufficient; though it need not be, provided decimals were used, a plan which does not seem to be contemplated by the Committee. The suggestion is even made that "it would be possible to carry the analysis still farther by means of symbols, such as ψ, κ, and so forth, to indicate physical properties, crystalline form, &c." The writers of this review venture to suggest that when the Greek alphabet is exhausted the Hebrew will come in handy.

This mixture of numerical symbols with word-headings is again resorted to in division "0930 Operations in Inorganic Chemistry," where it is suggested that "entries shall be made under significant headings, such as dissolution (*sic*) and solvents, crystallisation, distillation, . . . oxidation, electrolysis, furnace operations, &c., arranged alphabetically."

To organic chemistry the symbol 1000 is assigned, under which all entries shall be arranged that relate to the subject generally; substitution derivatives of the compounds included in each of the numbered divisions—especially haloid and allied derivatives—shall, as far as possible, be entered under the compounds from which they are derived.

The next paragraph provides that "entries under the name of a substance may, if necessary, be sub-divided in the same way as that proposed for inorganic substances."

Hydrocarbons receive the numerical symbol 1010, and the scheme for indicating their substitution derivatives, leads to amazing propositions; the general group is divided thus:—

1010 Hydrocarbons.
1020 Paraffins.
1030 Unsaturated Open-chain Hydrocarbons.
1040 Benzenoid Hydrocarbons.
1050 Reduced Benzenoid Hydrocarbons (Terpenes, &c.).
1060 Unclassified Hydrocarbons.

"Each of these divisions shall be sub-divided (excepting 1010 and 1020) into isologous groups, in each of which compounds shall be entered in homologous order. Then follow two new arbitrary signs for distinguishing derivatives; these are full-faced numerals, **2**, **4**, &c., used to indicate homologous series C_nH_{2n-2}, C_nH_{2n-4}, and the full-faced letter **C**, with exponents attached, to indicate the number of carbon atoms in a given compound.

Applying this scheme to nitropropane,—

$$CH_3.CH_2.CH_2.(NO_2),$$

it will receive the registration symbol $1020.C_3.NO_2$; allene, $C_2{:}C{:}CH_2$, will be indicated by the symbol $1030.2.C_3$, and bromotoluene, $C_6H_5.CH_2.Br$, will be indicated by $1040.6.C_7.Br$.

This plan of assigning to definite chemical bodies arbitrary symbols resembling in structure well-established formulæ is most objectionable; if carried out it would prove vexatious to chemists and of no practical value to librarians.

To alcohols and ethers the symbol 1100 is assigned; to acids, 1200; each of these groups is sub divided exactly as are the hydrocarbons, but the symbols of the sub-divisions do not harmonise. Since paraffins = 1020, "ols should have been 1120, and acids 1220 (instead of 1110 and 1210).

In the paragraph on acids, provision is made for indicating the number of oxygen atoms, the character of the acid, and the basicity by numbers, to which ol, al, on, id, or cy shall be appended, according to the origin of the acid. "Thus lactic acid would be marked $1210.C_3O_3$ (1.ol), and protocatechuic acid $1230.8.C_7O_4$ (1.2.ol)." Here, again, we have registration symbols resembling in a general way chemical formulæ, yet they do not show the constitution nor even suggest the name of the substance.

Number 1440 is given to carbohydrates other than mono-, di-, and trisaccharides, and 1450 to glucosides, and 1460 to resins, and it is provided that compounds belonging to these divisions shall be entered alphabetically; this is again a departure from the numerical plan. Another rule provides that "under alkaloids (1800) a list shall be given of vegeto-alkaloids, together with the Latin names of the plants from which they have been obtained, arranged in the alphabetical order of the plant names." Chemists not versed in botany would find this arrangement a puzzling one. Again, "alkaloids derived from plants (1810) and from animals (1820) shall be arranged alphabetically."

Division 2000 is styled "Coloured compounds" [!], a singular misnomer for compounds used in dyeing; yet another division, 2010, is called "Coloured substances, not dye-stuffs," and division 2020 is named "dye-stuffs." Provision is made for sub-dividing these categories thus:—

"2010 into Hydrocarbons (coloured), Alcohols (coloured), Ketones (coloured), &c.; 2020 into Azo dyes . . . dye-stuffs of vegetable origin, unclassified dyes," arranged alphabetically in each sub-division.

The rules concerning the entries of the sub-divisions of 3000, Analytical Chemistry, also lack uniformity, clearness, and exactness; "division 3200 shall include all entries relating to the determination of individual elements in their compounds and in mixtures, excluding determinations of atomic weights" which belong to division 3500 (theoretical and physical chemistry). Division 3300 shall include all entries relating to the determination of individual compounds, *e.g.*, alkaloids, carbohydrates . . . but excluding gases. If necessary gravimetric, volumetric, electrolytic, physical, &c., methods may be distinguished by letters, such as *g*, *v*, &c." "Division 3400 (Applied Analysis) shall include all entries relating to the analysis of composite materials, such as drugs, foods, soils, waters, and technical products generally, arranged under appropriate significant headings."

The remaining divisions, 3500, Theoretical and Physical Chemistry, and 4000, Physiological Chemistry, must be passed; the specimens given are sufficiently numerous.

A study of this remarkable scheme of classification shows that the Committee failed to recognise the fact that classification and notation are two distinct things, and that a notation need have no relation to the character of the class to which the notation is given. To differentiate the houses in a city, street and number are given; "120 Grand Avenue" suffices to distinguish a given house, and it is not necessary to construct a symbol indicating the number of stories, the number of windows, and the colour of the paint in order to recognise the address.

Accompanying the schedule of classification is a specimen page giving illustrations of the way in which these rules should be applied; the examples bring out forcibly the absurdities of the conglomerate method proposed. The paper on Argon, by Lord Rayleigh and W. Ramsay, receives the kabbalistic formula "0100.$\beta.\phi$," but if we understand rightly the Committee's rules, the numerals should be 0130, which stands for argon.

An article by J. J. Sudborough and L. L. Lloyd, on "Stereoisomerism as affecting formation of etheral salts from unsaturated acids," is assigned simply the number 3500; when, however, the same paper is entered under a different title, namely, "Etherification of stereoisomeric unsaturated acids a criterion of structure," it has the number 1200 γ; when, on the other hand, this paper is catalogued as: "Cinnamic and allied acids as a criterion of structure, Etherification of," the catalogue slip must bear the symbol 1230.10.$C_9O_2\delta$.

To a chemist the formula of cinnamic acid $C_6H_5.CH:CH_2.CO_2H$ has a definite meaning, and we protest against a system that introduces symbols, analogous in appearance, yet wholly misleading as respects the composition.

An examination of the schedule of classification of Chemistry proposed by the International Catalogue Committee shows that it consists of a medley of several methods. The system includes:—

1. Numbers, full-face, and inferiors, used for several distinct purposes.
2. Roman capitals, to denote component elements.
3. Roman lower-case, to denote kind of chemical process.
4. Italic letters in parenthesis, to denote basicity of acids.
5. Greek lower-case letters.
6. Word-headings arranged alphabetically.
7. Special provisions; exceptions to rules.

In 1772, at Ulm, was printed a thin octavo, having the title "Medicinisch-chymisch und alchemistisches oraculum," which contains a key to over two thousand symbols and kabbalistic figures found in alchemical manuscripts and books; the book is curious and instructive, as well as really serviceable to antiquarian chemists. The number of synonyms for a given substance is large; alum has twenty-six; aqua fortis, twenty-two; mercury, thirty-eight; a pound weight, eight, and cream of tartar is credited with thirty-two; the symbols have an uncouth appearance, but are hardly more fanciful than those proposed by the Committee on the International Catalogue. Should their schedule of classification prevail, a new edition of the "Alchemical Oracle" would soon become a necessity.

THE PARENT-ROCK OF THE DIAMOND IN SOUTH AFRICA.*

By Professor T. G. BONNEY, D.Sc., LL.D., V.P.R.S.

So much has been written on the occurrence of diamonds in South Africa that a very few words may suffice as preface to this communication. References to many papers on the subject are given in "The Genesis and Matrix of the Diamond" (1897), by the late Professor H. Carvill Lewis,† and others have been published since that date.‡ It may suffice to say that the diamond, first discovered in 1867 in gravels on the Orange River, was found three years later in certain peculiar deposits, which occur locally in a region where the dominant rock is a dark shale, sometimes interbedded with hard grits, or associated with igneous rocks allied to basalt. These deposits occupy areas irregularly circular in outline, and bearing a general resemblance to volcanic necks. The diamantiferous material, near the surface, is soft, yellowish in colour, and obviously much decomposed; at a greater depth it assumes a dull greenish to bluish tint, and becomes harder. At the well-known De Beers Mine, near Kimberley, the works in 1898 had been carried to a depth of about 1500 feet, and the diamantiferous material, for at least the last 100 yards, was not less hard than an ordinary limestone. It has a brecciated aspect, the dark, very minutely granular, matrix being composed mainly of serpentine (about four-fifths of the whole), and of a carbonate of lime (with some magnesia and a little iron). In this matrix are embedded grains of the following minerals:—Olivine, enstatite, smaragdite, chrome-diopside (omphacite of some authors), a brown mica, garnet (mostly pyrope, but more than one variety observed), magnetite, chromite, ilmenite, with several other minerals much more sparsely distributed.

Rock fragments are also present, variable in size, but commonly not exceeding about an inch in diameter, as well as in quantity. These occasionally, but not generally, are rather abundant. In some cases they are chips of the neighbouring black shale, but in others they are greyish-coloured with a somewhat porcelainised aspect. The latter are generally sub-angular in form, and externally banded or bordered with a darker tint; crystalline rocks have also been noticed, though these appear to be far from common, such as granite, diorite, and varieties of eclogite.§ As to the genesis of the diamond, more than one opinion has been expressed. Professor Lewis regarded the matrix as a porphyritic form of peridotite, once a lava, now serpentinised,‖ in which the diamond had been formed by the action of the molten rock on some carbonaceous material (probably the Karoo shale). Others

* A Paper read before the Royal Society, June 1, 1899.

† Edited by the present writer.

‡ Jules Garnier, *Geol. Soc. South Africa Trans.*, 1897, p. 91; H. S. Harger, *ibid.*, p. 124. See also W. G. Atherstone, *ibid.*, 1896, p. 76; L. De Launay, *Compt. Rend.*, 1897, cxxv., 335. The last author, in "Les Diamants du Cap" (Paris, 1897) gives a very full account of the mines, but an even better one will be found in Max Bauer, "Edelsteinkunde" (Leipzic, 1896, p. 208).

§ A. W. Stelzner, "Sitzungsber. u. Abhandl. der Isis" (Dresden), 1893 (April), p. 71, calls attention to the fact that these show signs of attrition and that they range in size from a few cubic millimetres upwards, being sometimes large boulders. Among the materials (at Kimberley) he mentions both granite and eclogite.

‖ For the rock itself he proposed the name "kimberlite."

regarded the matrix as a true breccia, comparing it with the agglomerates in volcanic rocks. But among the latter, some thought that the diamond had been produced *in situ* by the action of steam or hot water in a subsequent solfataric stage of the volcano, while others (including myself) held that it had been formed, like the garnets, pyroxenes, &c., in some deep-seated holocrystalline mass which had been shattered by explosions.*

The specimens which I am about to describe were obtained at the Newlands Mines, West Griqualand; from 40 to 42 miles from Kimberley, almost due N.W. Here the workmen occasionally came across well-rounded boulder-like masses of rather coarsely crystalline rock, studded with garnets, which are sometimes about a foot in diameter. Specimens of these were found or obtained by Mr. G. Trubenbach, the London manager of the Newlands Diamond Mine Company, during a visit to the mines in 1897. His interest had already been aroused by picking up a specimen, presently to be noticed, in which some small diamonds occurred, very closely associated with a garnet; so the boulders were brought back by him to England. On careful examination a small diamond was detected on the surface of one of these. On breaking the boulder others were revealed. The most interesting fragment was sent by Mr. Trubenbach to Sir W. Crookes, who showed it to me. Examination with a hand lens convinced me that the rock could not be a concretion of the "blue ground," but was truly holocrystalline and allied to the eclogites. Sir W. Crookes generously waived his own claim to study the specimen, and obtained for me permission from Mr. Trubenbach to have slices cut from it. I gladly take this opportunity of expressing my gratitude to both gentlemen; to Sir W. Crookes for allowing me to carry out this interesting investigation, and to Mr. Trubenbach for his great liberality in placing at my disposal a considerable suite of specimens (including other boulders) from the Newlands mines, and for the trouble which he has taken in affording me the necessary information.

Prior to the discovery, just mentioned, one or two instances had occurred at the De Beers Mine of a diamond apparently enclosed by or projecting into a pyrope. One such, the garnet being the size of a rather large pea, is in the collection at Freiberg (Saxony), to which it was presented in 1892.†

The specimen found by Mr. Trubenbach at the Newlands mine was a piece of blue ground, with a pyrope projecting from one angle. A small, apparently broken, diamond seems embedded at the top. The others (five) are well crystallised, two on one side, three almost in contact on the other. The pyrope (which has a kelyphite rim) seems to be indented by two, but to have once included the others, as they are in contact with the unaltered mineral. We were thus brought so far as to associate the diamond with the pyrope; though this proved no more than the presence of garnets in the parent rock of the diamond, and thus made the eclogite (already known to occur) highly probable, for, as observed by Professor R. Beck,‡ the specimen itself is blue ground. In confirmation of his statement I pulverised a fragment,§ and find that the powder corresponds with the matrix of the blue ground when similarly treated. The latest discoveries enable me to complete the chain of evidence.

Eclogite Boulders containing Diamonds.

The first named, that containing several diamonds, is a fragment (perhaps from a quarter to a third) of a boulder, which probably was ellipsoidal in shape, two of the axes being nearly equal and the third distinctly the longest. We may infer that it was rounded from a roughly rectangular block, since the curved surfaces are slightly flatter in the middle parts. The axial lengths in the fragment (prior to removing a piece from one end) were approximately 4 in. by 3 in. by 2 in. The rock is coarsely granular, apparently composed of two green-coloured minerals, one darker than the other (possibly only different states of a single mineral), and of rich resin-pink coloured garnets, varying in size from a hemp-seed to a pea, with slightly irregular distribution. The outer surface of the boulder, except for a very small "step" on one side, is smooth, the garnets barely, if at all, projecting. The latter are covered with a rather soft, dark skin, sometimes slightly thicker than the thumb nail, which often has partly fallen off. This, as can be seen on the broken surfaces, becomes less conspicuous in the inner part of the boulder, and is sometimes invisible to the unaided eye. Two small diamonds are exposed on the curved outer surface, one about half, the other about one-fifth of an inch from the edge of the cross fracture. On the latter surface, nearly an inch below the last named, three small diamonds appear to lie in a line touching one another, and near them are two others,* all four within a space about three-quarters of an inch square; an eighth diamond is about an inch and a half away (on the same face); a ninth, about one-fifth of an inch from the top edge; and a tenth occurs on the larger cross-fractured surface, but near to the edge of the other one. These diamonds are octahedra in form, generally with stepped faces—one, at least, apparently twinned—perfectly colourless, with brilliant lustre; the largest being quite 0·15 inch from apex to apex, the smallest not exceeding 0·05 inch. All seem to be embedded in the green part of the rock. As the outer part of the boulder looks rather more decomposed than the inner, I had a piece removed from one end, thus enabling me to study the mass to a depth of more than an inch from the surface, and examined a strip, about 4 inches long, in a series of five slices.

The late Professor Lewis has given, in the volume already mentioned, so full an account of the minerals which occur in the "blue ground," that it will be needless on the present occasion to do more than refer to his descriptions,† only calling attention to any variations in the mineral constituents and their association in these eclogites. These constituents are:—

1. (*a*) *Garnet* (Pyrope).—In the slice these appear a light tawny or yellowish red tint, retaining this tint (though much lighter) under the microscope.‡ They are generally clear, with frequent and irregular cracks, but are occasionally traversed by wavy bands of minute enclosures of a pale brown filmy mineral, which is rather irregular in outline, very feebly pleochroic, and gives with crossed nicols fairly bright polarisation tints. Similar minerals sometimes have formed along the cracks. They are probably mica, or possibly chlorite, and indicate incipient decomposition. The garnets towards the outside of the boulder, as already said, are enveloped in a "skin," and the microscope shows that it usually exists inside, though there it is thinner. In the former case it is generally browner in colour and more distinctly crystalline, corresponding in cleavage, pleochroism, &c., with a mica of the biotite group; in the latter it is greener and more filmy with an aggregate habit, and seems to project into the garnet. I regard it as due to decomposition, a form

* In other words, that the volcano (as occasionally has happened) had ejected little or no lava or scoria, discharging only steam and hot water, with shattered rock. This view is held by Max Bauer, in "Edelsteinkunde," p. 225, which, however, I had not seen when this paper was written.

† A. W. Stelzner, "Sitzungber. der Isis zu Dresden," 1893, s. 85, and R. Beck, *Zeitsch. f. Praktische Geologie*, 1898 (May, p. 163).

‡ *Ut suprà.*

§ I could not advise Mr. Trubenbach to have a slice cut from the specimen, as I feared it might be injured, but he kindly detached a little fragment from the opposite end to that named above, which I have thus examined.

* It is possible that these two form a twin crystal, but I think they are separate. As the point is unimportant, I have not attempted to clear away the matrix.

† We must also not forget the paper by Professor Maskelyne and Dr. Flight (*Quart. Journ. Geol. Soc.*, vol. xxx., p. 406), in which several of these minerals are described, analysed, and identified. In fact, the authors ascertained everything that was possible with the materials then obtainable.

‡ Unless it is expressly stated, the use of a 1-inch objective may be assumed.

of the well-known kelyphite rim, sometimes a mica, sometimes a chlorite, possibly now and then associated with a little minute hornblende. In a few cases a "rim" is brown in the outer part and green within. The constituents tend to a parallel rather than a radial grouping. The garnets occasionally contain minute branching root-like enclosures grouped in bands. Though these act on polarised light, I regard them as empty cavities, and attribute this to diffraction.

cracks, is often converted into a minutely granular to fibrous mineral, which gives a "dusty" aspect to that part of the crystal when viewed with transmitted light, and a whitish-green one with reflected light. This often terminates in a minutely acicular fringe, piercing the original diopside. Its grains occasionally are a little larger, showing a cleavage, dull green in colour, fairly pleochroic, and having the extinction of hornblende. A process of secondary change, as in uralite, is no doubt

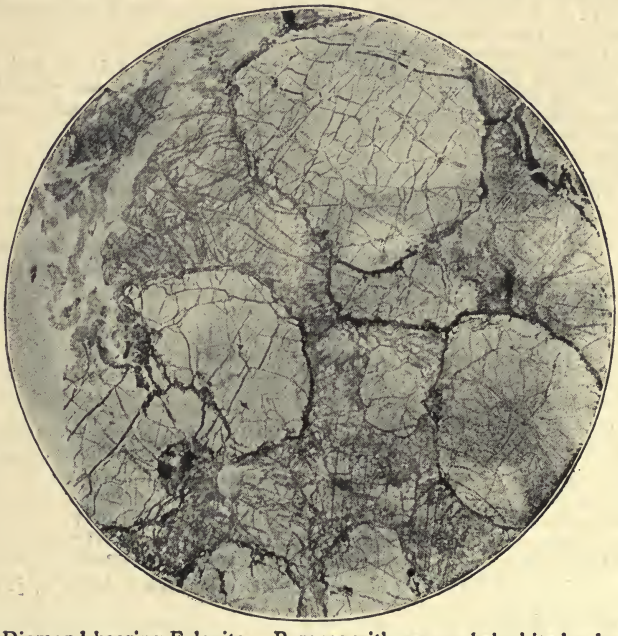


Fig. 1.—Section of the Diamond-bearing Eclogite. Pyropes with narrow kelyphite borders, and chrome diopside intercrystallised. The clinopinacoidal cleavage of latter visible in the lower part of the section.

(*b*) *Chrome-diopside.* — The mineral described under that name by Professor Lewis, and referred to by others as omphacite or sahlite. The individuals are sometimes about a quarter of an inch long. In thin slices it is a pale dullish green colour, inclining to olive; under the microscope, a pale sea-green, with a trace of pleochroism. It has one strongly marked cleavage, not, however, nearly so close as in ordinary diallage, and a second weaker,

Fig. 2.—Garnet and Diamond (diagrammatic, nearly twice natural size). (1) Diamond, (2) garnet, (3) kelyphite rim.

sometimes approximately at right angles to it.* On examining flakes, obtained by crushing, I find the strong cleavage to be clinopinacoïdal and the other probably basal, and obtain on a clinopinacoïd an extinction of 35° with a prism edge. It is, in fact, identical with the pyroxene described by Professor Lewis† as chrome-diopside. In it (though rarely) small rounded enclosures of a greenish mineral aggregate much blackened with opacite. I regard them as alteration products of a ferriferous olivine. This diopside, at the exterior and along indicated. Now and then a tiny film of brown mica occurs in this part or even in a crack in the diopside.

It is this alteration product which gives the mottled aspect mentioned above as visible to the unaided eye, so this is not indicative of a third important constituent in the original rock. In one of the slices the mica just named attains a larger size (about 0·03 inch across), has a fairly idiomorphic (hexagonal prism) outline, and is not restricted to the margin of the garnet. In this case it is generally associated with calcite,* which it tends to surround, and that in one place encloses a radiating acicular mineral (? a zeolite), in another the calcite, or some other carbonate, is mixed with a serpentinous material. Distinct granules of iron oxide are practically absent from the slices, though here and there it may be indicated by some opacite. I have not found spinel, or rutile, or zircon, or pseudobrookite. In fact, putting aside the diamonds, the rock in its unaltered condition was a coarsely holocrystalline mixture of chrome-diopside and garnet, with a few small enclosures of olivine,—in other words, it was a variety of eclogite and of igneous origin.†

2. A fragment (probably about one quarter) of a flattish ovoid boulder.—The two broken surfaces, which are

* One may give a general idea of their relative importance by comparing them to the columns and cross-joints in some basalts.

† *Loc. cit.*, p. 21.

* From the facts I think it probably of secondary origin. It reminds me sometimes of the brown mica produced by contact metamorphism.

† I am, of course, aware that eclogite, in the past, has been regarded by some geologists as a metamorphic rock. Apart from the fact that several rocks once assigned to this class are now, with good reason, regarded as igneous, I have had several opportunities of studying eclogite, and have no doubt as to its origin. Take away the alkali from a magma with the chemical composition of a diorite, and the result would be garnets in place of felspar, *i.e.*, an eclogite.

nearly at right angles, measure 5 and 5½ inches, roughly, and it is about 3¼ inches high. The rock very closely resembles the one just described, except that mica occurs rather oftener and in larger flakes; perhaps the garnets (here also not quite regularly distributed) are slightly more numerous. The outer surface is not quite so well preserved, though enough remains to show that it also has been smooth, and a few thin veins of a white mineral (calcite?) traverse the rock. On this surface, near the meeting of the two fractures, and exposed by the removal of a little material (*i. e.*, it might originally have been just hidden) is a diamond (octahedron), apparently about 0·1 inch in diameter. On one side it rests against a pyrope, the adjacent surface of which is incurved, the two minerals being parted by the dull green-coloured kelyphite rim of the latter, which is about 0·03 inch in thickness. Thin sections of this boulder correspond almost exactly with those from the other, the garnets showing precisely the same tints, though traces of a cleavage (roughly parallel throughout) are perceptible on close inspection, and are distinct under the microscope. In garnet such a structure commonly indicates pressure, and the general parallelism accords with this explanation, but the other constituents show no signs of crushing. The "kelyphite" rims to the garnets are perhaps slightly broader, and the brown mica passes into a green (chloritic?) mineral, and occupies cracks in the garnet a little more frequently, but, as before, the constituents tend to lie parallel rather than radially. One or two of the diopsides show fine oscillatory twinning. The cracks are occupied with calcite or some altered carbonate. There is no real difference between this eclogite and the last-named one.

(To be continued(.

ELECTROLYTIC SEPARATION OF CHLORINE, BROMINE, AND IODINE.

By H. SPEKETER.

The electromotive forces necessary for the electrolytic decomposition of the halogen acids are the following:—HCl = 1·31 volt, HBr = 0·94 volt, HI = 0·52 volt. Attempts made to separate the halogens by successively increasing the electromotive force from its lowest to its highest power have not been attended with satisfactory results.

Iodine, for example, has not been completely separated from the other halogens, even when increasing the electromotive force to 1·2 volts and removing the iodine formed by means of sulphide of carbon. This want of success appears to be due to the diffusion of the free iodine towards the cathode, where it is re-converted into hydriodic acid. We can, however, effect a quantitative separation by using a platinum cathode and an anode of perfectly pure silver. Under these conditions, the electromotive force of the decomposition can be calculated by Nernst's formula. The electrolysis is carried out in normal sulphuric solution. The iodine is precipitated in the form of iodide of silver on the anode when the strength of the current is below 0·13 volt, and the bromine when it is below 0·35 volt. As for the chlorine it is preferable to determine it in the ordinary manner by Volhard's method.

To effect the electrolysis, a thermopile of constant electromotive force is preferable, and a resistance-bar should be placed in the circuit so that the current may be regulated at will.

The vessel in which the electrolysis is carried out is a narrow test-tube fitted with a platinum cathode and an anode of pure silver foil.

During the whole time of the operation a current of hydrogen should be passed through the liquid for the purpose of clearing away any air or oxygen from the cathode. If this precaution be not taken, bromide and chloride of silver will be precipitated on the anode at the same time as the iodide. In fact, in a solution of the halogen acids, the silver gives off hydrogen at the cathode, and if this hydrogen is continually eliminated by oxygen and air the haloid salts of silver will be deposited at the anode even without the use of any current at all.

A sensitive galvanometer in the circuit will show the exact moment when each halogen is completely eliminated from the solution.

The precipitate on the anode must be carefully washed and dried at 120°. The results given in the following tables will enable an idea of the exactitude of this method to be formed.

I.—*Separation of Iodine and Chlorine. Difference of Potential* = 0·13 *volt.*

Iodine used. Grm.	Iodine found. Grm.	Iodine used. Grm.	Iodine found. Grm.
0·29087	0·2892	0·1588	0·1598
0·0481	0·0480	0·2290	0·2565
0·3807	0·3773	0·15437	0·1532
0·2394	0·2386		

II.—*Separation of Bromine and Chlorine. Difference of Potential* = 0·35 *volt.*

Bromine used. Grm.	Bromine found. Grm.	Bromine used. Grm.	Bromine found. Grm.
0·19437	0·1940	0·19625	0·1958
0·1062	0·1041	0·19047	0·1883
0·27354	0·2736	0·18994	0·1906
0·2122	0·2111	0·18651	0·1836

III.—*Separation of Iodine and Bromine. Difference of Potential* = 0·13 *volt.*

Iodine used. Grm.	Iodine found. Grm.	Iodine used. Grm.	Iodine found. Grm.
0·17066	0·1685	0·1078	0·1080
0·1636	0·1610	0·1235	0·1218
0·2029	0·2036	0·1356	0·1348

—*Zeit. für Elektrochem.*, v., [23], p. 539.

THE ESTIMATION OF TARTARIC ACID IN THE PRESENCE OF CITRIC ACID.

By A. BORNTRÆGER.

The author shows that a solution containing 10 grms. of KCl and 2·5 grms. of neutral anhydrous citrate of potash in 100 c.c. of water, completely dissolves 1 grm. of bitartrate of potash at the ordinary temperature, while the solubility of the bitartrate is much less if the neutral citrate is replaced by 2·5 grms. of citric acid. If the 10 per cent solution of KCl contains both 2·5 per cent of neutral citrate and 2·5 per cent of citric acid the solubility of the bitartrate is still less.

In the analysis of lemon-juice we take 20 grms. of the sample (containing 16 to 17 per cent of the mixed acids), dissolve in water, neutralise with caustic potash, add 5 grms. of KCl, and dilute to 50 c.c. We then add 5 grms. of a 50 per cent solution of citric acid, and shake until the precipitate of bitartrate of potassium commences to appear; the whole is then allowed to stand for a night; filter off the bitartrate, wash first with a 10 per cent solution of KCl which has only just been saturated with bitartrate of potash, then with a solution of pure KCl. The precipitate is then dissolved and titrated.

The author has studied the effects of variable proportions of the two acids, and has arrived at the following conclusions:—

1. By using 5 grms. of citric acid as precipitant satisfactory results were obtained (97·3 per cent to 101·3 per cent) when the neutralised solution contained 1 grm. of bitartrate + 0·5—4 grms. of citric acid, 3 grms. of bitartrate + 3—4 grms. of citric acid, or 4 grms. of bitartrate + 3—5 grms. of citric acid.

2. By using 3 grms. of citric acid as precipitant satisfactory results are obtained (97·3 to 101·4 per cent) when the neutralised solution contained 1 grm. of bitartrate + 0·5—1 grm. of citric acid, 2 grms. of bitartrate + 0·5—2 grms. of citric acid, or 3—4 grms. of bitartrate + 1—2 grms. of citric acid.

With a larger proportion of bitartrate with regard to the citrate, the results are too high on account of the precipitation of a difficultly soluble acid citrate. When we have to deal with a solution containing both tartaric and citric acids, it is necessary to take such a quantity of citric acid corresponding to 3 grms. of acidity (citric), then add 5 grms. of KCl, neutralise with potash, dilute to 50 c.c., and precipitate as already described with 3 to 5 grms. of citric acid. If the proportions of the two acids do not come within the above limits, a fresh estimation must be made, and the proportions regulated by adding, according to the case, citric acid or a known weight of tartaric acid.—*Zeit. Anal. Chem.*, xxxvii., [8], 477.

ON A NEW METHOD FOR THE ESTIMATION OF FORMIC ALDEHYDE.

By O. BLANK and H. FINKENBEINER.

The old method of estimating formic aldehyde which consisted of titrating the solution with ammonia, and which was in general use, gave results varying considerably from those given by methods now practised. These give very concordant results, and for solutions containing from 20 to 40 per cent of formic aldehyde, figures which are about 1·5 per cent higher than those given by the ammonia method.

The new method, which is based on the oxidation of formic aldehyde into formic acid by peroxide of hydrogen in alkaline solution, and the titration of the excess of alkali, is quite as exact as the commercial methods just mentioned. The estimation is conducted as follows: 3 grms. of the solution of formic aldehyde under examination (or 1 grm. in the case of solid formic aldehyde) are weighed out carefully and placed in a tall conical flask containing 25 c.c. of double normal soda (30 c.c. when the concentration of the formic aldehyde is greater than 45 per cent). The mixture is then immediately treated with 50 c.c. of peroxide of hydrogen at from 2·5 to 3 per cent; in the case of the peroxide of hydrogen having an acid reaction, the acidity should be determined and deducted from the final result. The peroxide of hydrogen must be added gradually (taking about three minutes) by means of a funnel; after two or three minutes the funnel is rinsed with water, and the excess of alkali is titrated with a double normal solution of sulphuric acid; in very exact analyses the water used for rinsing should be boiled first to drive off any carbonic acid. Litmus is used as an indicator (Portes Ruyssen, *Zeit. f. Anal. Chem.*, xvi., p. 25; *Gazz. Chim. Thal.*, xx., p. 394).

If we have to deal with solutions containing less than 30 per cent of formic aldehyde the mixture should be allowed to stand for about ten minutes after the addition of the peroxide of hydrogen, for the reaction to be complete.

The centesimal contents of formic aldehyde is obtained directly by multiplying the number of c.c. of soda employed in the titration by 2 if 3 grms. of the solution was originally taken, or by 6 if we took 1 grm. of the solid formic aldehyde.

The reaction takes place with the disengagement of a considerable amount of heat and production of froth. It corresponds to the following equation—

$$2H.CHO + 2NaOH + H_2O_2 = 2H.COONa + H_2 + 2H_2O.$$

We are not able to say whether the reaction takes place quantitatively in the manner indicated, or whether there is a further oxidation of the formic acid into carbonic acid, $H.CHO + NaOH + H_2O_2 = H.COONa + 2H_2O$.

We did not consider it necessary to estimate the hydrogen set at liberty, as a part of it would no doubt combine with the excess of peroxide of hydrogen. The presence of hydrogen was, however, proved by the inflammability of the gas given off, and by the explosion of a mixture of this gas with air. After removing the excess of peroxide of hydrogen, the formic acid can be easily estimated by nitrate of potash in the usual manner.*

A mixture of 0·5 grm. of formic aldehyde, 5 c.c. of double normal soda, and 10 c.c. of peroxide of hydrogen was titrated after standing for half-an-hour, and then being gently heated on a water-bath with 10 grms. of nitrite of potash for half-an-hour. After adding 5 grms. of bichloride of mercury the mixture was digested for two hours in a flask fitted with a reflux condenser.

The following results were obtained:—

(*a*) 3·1267 grms. HgCl representing 39·8 per cent CH_2O
(*b*) 3·4941 " " " " 44·5 " " "

After oxidation by means of peroxide of hydrogen we found in the same manner (*a*) 39·7 per cent CH_2O, and (*b*) 44·5 per cent CH_2O.

Other methods in common use gave (*a*) 39·8 per cent CH_2O, (*b*) 44·5 per cent CH_2O.

We have used our method for the estimation of several other aldehydes—acetic aldehyde, paraldehyde, benzoic aldehyde, &c.

Acetic aldehyde reacts much more slowly than formic aldehyde with peroxide of hydrogen and caustic soda; but after half-an-hour an abundant disengagement of hydrogen takes place. We have still to decide whether this reaction is quantitative.

To be complete this reaction requires several hours. In the case of paraldehyde the action of the peroxide of hydrogen is even slower, but after the addition of a trace of ferric salt, the disengagement of gas was extremely slight though quite regular.

Benzoic aldehyde reacts a little more energetically, especially in the presence of a trace of ferric salt, but to be complete a considerable time is necessary. Even the addition of methylic alcohol—which is not attacked by peroxide of hydrogen under these conditions—to help the solution of the aldehyde did not notably accelerate the reaction.—*Berichte der D. Chem. Gesel.*, 1898, p. 2979.

ESTIMATION OF FAT IN ALIMENTARY PRODUCTS, MEAT, &c.

By L. LIEBERMANN and S. SZEKELY.

Boil 5 grms. of the substance for thirty minutes with 30 c.c. of a 50 per cent ($d = 1·541$) solution of caustic potash in a specially made flask, of which the following is the description:—The body of the flask must be 7·5 c.m. in diameter and 5·5 c.m. high, with a flat bottom; the neck must be 19·5 c.m. in length, and 3·5 c.m. in diameter throughout. When filled half way up the neck it should contain 290 c.c. A gauge mark must be made at 240 c.c.

After boiling, the contents of the flask are allowed to cool; 30 c.c. of alcohol at 90—94 per cent are then added, and the whole again heated for ten minutes. After cooling again 100 c.c. of sulphuric acid at 20 per cent ($d = 1·145$) are carefully added, while constantly stirring, the whole being kept cool to prevent the loss of volatile fatty acids. The solution, which will finally contain an excess of about 4·4 grms. of sulphuric acid, is now mixed with 50 c.c. of petroleum ether ($d = 0·6$ to $0·7$; and boiling point

* A blank experiment with nitrite of potash and bichloride of mercury showed that these two substances do not react under these conditions. It is only after the lapse of a very long time that a faint cloudiness can be noticed.

=60°); the flask must now be well corked and shaken up about 30 times at intervals of one or two minutes. A saturated solution of chloride of sodium is then added so as to fill the flask up to the middle of the neck, and make the level of the aqueous solution below the ether, near the 240 c.c. mark. Shake again several times, and place the flask in warm water.

As soon as the layer of ether (containing most of the fats) separates out, 20 c.c. are taken by means of a pipette, and transferred to a 150 c.c. flask with a wide neck. Add 40 c.c. of neutral alcohol at 96 per cent, and titrate with decinormal alcoholic potash. The solution is then again transferred to a tared covered glass crucible about 80 c.c. in diameter. Evaporate slowly to dryness on a water-bath, heat in an oven at 100° for an hour, and weigh. To calculate the amount of fat, it is necessary to deduct the amount of potash contained in the soap, and add the corresponding weight to the glyceric radical. As 1 c.c. of decinormal potash corresponds to 0·00391 grm. of potassium, and to 0·00136 grm. of C_3H_5, as many times 0·00255 grm. must be deducted as c.c. of potash have been used in the titration.

The amount of fat may then be calculated according to the formula—

$$F = \left[\frac{S - 0{\cdot}01 - (k \times 0{\cdot}00255)}{a}\right] \times 250.$$

in which F represents the percentage of fat present in the substance; S the weight of potash soap extracted from 20 c.c. of petroleum ether; k the number of c.c. of decinormal potash; and a the weight of the substance analysed.—*Arch. Physiol.*, lxii., 360.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 15th, 1899.

Professor T. E. THORPE, F.R.S., President, in the Chair.

MESSRS. A. R. Foulerton, S. B. Schryver, and J. P. de Castro were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Percy Kay, 3, Phene Street, Chelsea, S.W.; Hugh Main, 45, The Vicarage, Old Charlton, Kent.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

Robert Henry Aders, George Dekeyne Atkinson, Percy Bean, Walter Lionel Blackman, Wilfred Carpmael, James Connah, B.Sc., Henry Meldola Danziger, Frederick Doyle, Frederick Charles Dunscombe, William Frederick Eichenauer, F. N. Ashcroft Fleischmann, William Gordon Fraser, Frederick Hutton Getman, Julius Hübner, Edward Charles Johnson, Arthur Alexander Leon, James McAlley, Kobert McClumpha, George Alfred Parkes, Stanley John Peachey, Eskricke Sidney Phillips, B.A., Sidney Rossiter, Henry Royal-Dawson, William F. John Shepheard, John William Shepheard, B.Sc., Charles Simmonds, B.Sc., John Ward Stainer, Samuel Stansfield, B.Sc., George Hardstaff West, B.Sc., Christopher Joseph Whittaker.

Of the following papers those marked * were read:—

*84. "*On the Decomposition of Chlorates, with special reference to the Evolution of Chlorine and Oxygen.*" By W. H. SODEAU, B.Sc.

Some chlorates, on being heated, give off almost all their chlorine as such, whilst other chlorates give none. According to Schulze, the chlorate breaks up into chloride and oxygen, the chlorine evolved being due to the nascent oxygen attacking the chloride, whilst Spring and Prost regard the chlorate as decomposing into oxide, chlorine, and oxygen, the chlorine being more or less re-absorbed. The author points out that in addition to these two theories two others are possible: (1) that chlorates may break up in both of these ways simultaneously, and (2) that chloride and oxide may represent the balanced action of chlorine and oxygen.

His experiments have been made chiefly with potassium and barium chlorates. The former gives no chlorine, whether the pressure of the evolved gas be kept at 1 m.m. or at 1 atmosphere. With barium chlorate, however, 0·066 per cent of the total chlorine was evolved when the pressure was kept at 1 to 2 m.m., and the duration of the experiment 233 minutes, whilst at atmospheric pressure, 0·093 was obtained when the duration was 165 minutes, but when very rapidly decomposed (half a minute), the percentage of chlorine evolved rose to 0·705. These are the averages of several experiments.

From the results of his experiments, the author concluded that when barium chlorate is heated, it undergoes two decompositions at the same time: (*a*) an exothermic decomposition into chloride and oxygen, (*b*) an endothermic decomposition into oxide, chlorine, and oxygen, and that no appreciable reaction takes place between the chloride and oxygen (or chlorate), or between the oxide and chlorine, but that the increase of chlorine in a rapid decomposition may be ascribed to the great rise of temperature favouring the endothermic reaction. He believed that potassium chlorate decomposed directly into chloride and oxygen. Further experiments were being conducted on the behaviour of manganese oxides with potassium chlorate, and on the decomposition of pure lead and calcium chlorates. The experiments already performed with these chlorates appear to confirm the author's view that these two independent reactions occurred.

*85. "*Action of Hydrogen Peroxide on Formaldehyde.*" By A. HARDEN, M.Sc., Ph.D.

When solutions of hydrogen peroxide and formaldehyde are mixed, no reaction appears to take place, but when the liquid is made strongly alkaline with soda, hydrogen is evolved. The reaction occurs according to the equation $H_2O_2 + 2CH_2O + 2NaOH = 2H{\cdot}CO_2Na + H_2 + 2H_2O$. Hydrogen peroxide, therefore, when treated with alkaline formaldehyde, gives a volume of hydrogen exactly equal to the volume of oxygen which it would give with potassium permanganate and sulphuric acid.

The reaction proceeds slowly and incompletely unless a large excess of alkali be present. When hydrogen peroxide is treated with excess of formaldehyde, the reaction takes place rapidly and completely, and the hydrogen which is evolved is pure. When, on the other hand, formaldehyde is treated with excess of hydrogen peroxide, the reaction is incomplete and proceeds very slowly, whilst the gas evolved contains oxygen. Hence the reaction does not appear adapted for the quantitative estimation of formaldehyde in aqueous solutions.

Cuprous oxide and soda give a somewhat similar reaction with formaldehyde. This reaction was described by Loew (*Ber.*, 1887, xx., 145) as a catalytic reaction, but it appears in reality to be a quantitative one, expressed by the equation—

$$Cu_2O + 2NaOH + 2CH_2O = Cu_2 + H_2 + 2H{\cdot}CO_2Na + H_2O.$$

Cupric oxide also gives a similar reaction, two atoms of hydrogen being liberated for each atom of oxygen in the oxide.

When caustic soda and then formaldehyde are added to a solution of copper sulphate and the liquid gently warmed, the cupric hydroxide is reduced to cuprous oxide without evolution of hydrogen, and when the temperature is subsequently raised, the cuprous oxide reacts as described above. When, on the other hand, caustic soda is added to a boiling solution of copper sulphate, the liquid cooled, and formaldehyde then added, no reduction to cuprous oxide occurs on warming, but metallic copper is formed, and twice as much hydrogen is evolved as in the previous case.

Manganese dioxide does not appear to be reduced by

formaldehyde, whilst the oxides of mercury and bismuth are reduced without evolution of hydrogen.

Discussion.

Mr. Cross said that he regarded the author's results as additional evidence that hydrogen peroxide tends to react as H_2O_2, as it was clear that, in this case, it could not react as H_2O,O.

Dr. Debus pointed out that, in acting as an oxidising agent, hydrogen peroxide usually broke up into water and oxygen, but since aldehydes in many reactions behave as hydrides, we might suppose that the equation $2H\cdot CHO+(HO)_2=2(HO\cdot CHO)+H_2$ represented the change, the hydrogen set free coming from the aldehyde.

*86. "*Homocamphoronic and Camphononic Acids.*" By Arthur Lapworth and Edgar M. Chapman.

a-Dibromocamphor, though scarcely affected by the ordinary mild oxidising agents, is rapidly attacked by dilute nitric acid in presence of silver nitrate. The greater portion of the substance is reduced to monobromocamphor and camphor, but a small quantity is converted into a neutral *nitro*-compound, $C_{10}H_{14}N_2O_6$, which crystallises in beautiful, orthorhombic prisms melting at 93—94°. A still smaller quantity of the dibromo-compound is converted into an *acid*, $C_{10}H_{16}O_6$, which is found to be identical with the substance obtained by Forster (*Trans.*, 1896, lix., 49) on oxidising bromocamphorenic acid with dilute permanganate. The authors find that this acid is tribasic, and for it they propose the name *homocamphoronic acid*; it is an open chain tricarboxylic acid, and its constitution must be represented by one of two formulæ, $CO_2H\cdot CMe_2\cdot CMe(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$ or $CO_2H\cdot CH_2\cdot CMe_2\cdot CMe(CO_2H)\cdot CH_2\cdot CO_2H$, of which the former seems to be the more probable. Homocamphoronic acid is optically active; in 2 per cent aqueous solutions $[\alpha]_D=-34{\cdot}96°$. It is somewhat sparingly soluble in water, and separates from aqueous solution in small prisms which give off water and melt, according to the rate of heating, between 180° and 208°, the latter temperature being probably the true melting point. *Anhydrohomocamphoronic acid*—

$$CO_2H\cdot C_7H_{13}\begin{matrix}CO\\CO\end{matrix}>O,$$

is made by heating the acid or by warming it with acetyl chloride; it crystallises in prisms melting at 86—87°. The aniline derivative, $(CO_2H)_2\cdot C_7H_{13}CO\cdot NHPh$, melts at 98—100°, and the paratoluidine derivative, $(CO_2H)_2\cdot C_7H_{13}\cdot CO\cdot NH\cdot C_7H_7$, at 163—164°.

When anhydrohomocamphoronic acid is heated to 200—260° it loses carbon dioxide and yields an acid having the formula $C_9H_{14}O_3$. This substance is a saturated cyclic ketonic acid having the structure—

$$\begin{matrix}CO\cdot CMe_2\\|\\CH_2\cdot CH_2\end{matrix}>CMe\cdot CO_2H \quad \text{or} \quad \begin{matrix}CH_2\cdot CMe_2\\|\\CO\text{---}CH_2\end{matrix}>CMe\cdot CO_2H,$$

and, therefore, containing the carbon atoms in the position assumed by Bredt and Perkin for nine of the ten atoms in camphoric acid. The substance is, in fact, identical with a ketonic acid obtained by J. Walker as a by-product in the electrolysis of ethyl allocamphorate. Dr. Walker was good enough to send the authors a small specimen of his acid for comparison, and the identity of the two substances has been completely established; he has, moreover, agreed to the name *camphononic acid*, which the authors propose for it. It melts at 228°, and has all the properties assigned to it by Walker. The phenylhydrazone, $CO_2H\cdot C_8H_{13}:N\cdot NHPh$, crystallises in colourless needles melting at 174°. The *bromophenylhydrazone*, $C_{15}H_{19}O_2N_2Br$, forms transparent prisms and melts at 194—195°. The *semicarbazone* crystallises in needles and melts and decomposes at 230—232°.

When camphononic acid is very carefully oxidised with dilute nitric acid, a large quantity of camphoronic acid, which is apparently the sole product, is obtained.

*87. "*Action of Silver Compounds on α-Dibromocamphor.*" By Arthur Lapworth.

The formation of homocamphoronic acid from *a*-dibromocamphor by the action of dilute nitric acid and silver nitrate is preceded by the production of an unsaturated acid, $C_{10}H_{15}BrO_2$, identical with bromocamphorenic acid, which was first obtained by the reduction of *a*-dibromocampholid (Forster, *Trans.*, 1896, lxix., 46). This substance may be obtained by heating a solution of *a*-dibromocamphor in acetic acid or alcohol with silver nitrate, acetate, or oxide; the amount formed is small, however (10—20 per cent), the greater portion of the dibromocamphor undergoing reduction.

The formation of bromocamphorenic acid appears at first to be due to hydrolysis, represented empirically by the equation $C_{10}H_{14}Br_2O+H_2O=C_{10}H_{15}Br_2+HBr$. As bromocamphorenic acid at once loses hydrogen bromide when treated with cold dilute potassium permanganate, and is subsequently converted into homocamphoronic acid, it seems certain that it contains the group $-CH{=}CBr-$ as a part of the closed chain; and as dibromocamphor contains the group $-CBr_2\cdot CO-$, it would appear that, in the formation of bromocamphorenic acid, these two carbon atoms are separated, and that one of them enters the second pentamethylene ring. Of the possible formulæ for bromocamphorenic acid, which are, of course, easily derived from the two possible formulæ for homocamphoronic acid (see preceding note) the formula—

$$CH\begin{matrix}CBr\cdot CMe_2\\CH_2\cdot CH_2\end{matrix}>CMe\cdot CO_2H$$

is the one which is most in accordance with the facts which have been observed, the corresponding formula for dibromocampholid being—

$$CHBr\begin{matrix}CBr\cdot CMe_2\\O\text{---}CO\\CH_2\text{---}CH_2\end{matrix}>CMe.$$

88. "*The Colouring Matter of Cotton Flowers.*" By A. G. Perkin.

The flowers of the cotton plant, *Gossypium herbaceum*, are employed as a dye-stuff in the Manipur district of India. They contain as glucoside a new colouring matter, *gossypetin*, $C_{16}H_{12}O_8$, soluble in alkalis with an orange-red colour, becoming green on oxidation. The *hexacetyl* compound, $C_{16}H_6O_8Ac_6$, colourless needles, m. p. 212—216°; the *sulphate*, $C_{16}H_{12}O_8,H_2SO_4$, the *hydriodide*, $C_{16}H_{12}O_8,HI$, orange-red needles, and the *monopotassium* salt, $C_{16}H_{11}O_8K$, a crystalline powder, have been prepared. Gossypetin contains no methoxyl groups, and on fusion with alkali yields phloroglucinol and protocatechuic acid. It is probably a member of the flavone group of colouring matters. Gossypetin is similar to, but not identical with, thujetin, which is present in *Thuja occidentalis* (Kawalier, *Jahresbericht*, 1858, 512).

Note on Rottlerine.—The decomposition products of rottlerine, $C_{33}H_{30}O_9$, a colouring matter of kamala, *Mallotus Philippinensis*, previously described (*Trans.*, 1893, lxv., 981; 1895, lvii., 230), are with fused alkali, acetic and benzoic acids, and with nitric acid *o*- and *p*-nitrocinnamic acids. It has now been found that fused alkali at 220—240° yields also phloroglucinol.

89. "*Experiments on the Synthesis of Camphoric Acid.*" By H. A. Auden, W. H. Perkin, jun., and J. L. Rose.

These experiments were instituted with the object of preparing an acid of the formula—

$$\begin{matrix}CO_2H\cdot \overset{*}{C}OH\cdot Me & H\overset{*}{C}(Me)_2\\|&|\\CO_2H\cdot CH\text{---}CH_2\text{---}&CH_2\end{matrix},$$

in the hope that it might prove possible to eliminate water between the points marked *, and thus obtain an acid,—

$$\begin{matrix}CO_2H\cdot C(Me)\text{---}&C(Me)_2\\|&|\\CO_2H\cdot CH\cdot CH_2\cdot&CH_2\end{matrix},$$

which would have the constitution first suggested by Perkin (*Proc.*, 1896, xii., 191) as a possible expression of the constitution of camphoric acid. Ethyl isoamylacetoacetate was dissolved in ether and treated at a low temperature with potassium cyanide and hydrochloric acid, when ethyl α-isoamyl-ββ-hydroxycyanobutyrate, $Me(CN)C(OH)\cdot CH(C_5H_{11})\cdot CO_2Et$, was obtained as a thick oil, which on hydrolysis with alcohol and hydrochloric acid, yielded as principal product methylhydroxisoamylsuccinimide,—

$$\begin{matrix} Me\cdot C(OH)\cdot CO \\ | \qquad\quad \end{matrix}\!\!>\!NH \text{ (m. p. 104°).}$$
$$C_5H_{11}\cdot CH\!-\!CO$$

This substance, when boiled with sodium carbonate, is first converted into the corresponding amide, which crystallises from water and melts at 183°, and then into αα'-methylhydroxy-α'-isoamylsuccinic acid,—

$$\begin{matrix} Me\cdot C(OH)\cdot CO_2H \\ | \qquad\quad \end{matrix},$$
$$C_5H_{11}\cdot CH\!-\!CO_2H$$

which melts at 66°, and yields a silver salt of the formula $C_{10}H_{16}O_5Ag_2$. As this acid has the constitution represented by the formula given at the commencement of this abstract, experiments were next made with the object of eliminating water in such a way as to obtain a saturated acid of the same composition as camphoric acid, but without success. When the acid is subjected to distillation, water is eliminated and an oil, distilling at 260°, is obtained, which after careful investigation has been found to be methylisoamylmaleic anhydride,—

$$\begin{matrix} Me\cdot C\cdot CO \\ \| \qquad\quad \end{matrix}\!\!>\!O.$$
$$C_5H_{11}\cdot C\cdot CO$$

This anhydride dissolves in potash solution, but on acidifying, the anhydride, and not the acid, separates, a behaviour which is exactly similar to the case of xeronic acid,—

$$\begin{matrix} Et\cdot C\cdot CO_2H \\ \| \qquad\quad \end{matrix},$$
$$Et\cdot C\cdot CO_2H$$

which, when set free from its salts, is obtained in the form of its anhydride.

The solution of methylisoamylmaleic anhydride in benzene gives, with aniline, the anil $C_{16}H_{19}O_2N$, which crystallises from methyl alcohol and melts at 70°. When the anhydride is reduced with hydriodic acid and phosphorus, it yields a mixture of *cis*- and *trans*-methylisoamylsuccinic acids,—

$$\begin{matrix} Me\!-\!CH\cdot CO_2H \\ | \qquad\quad \end{matrix},$$
$$C_5H_{11}\cdot CH\cdot CO_2H$$

the former of which melts at 92° and the latter at 142° (see following abstract).

Ethyl-isoamylacetoacetate is readily reduced by sodium amalgam, forming α-isoamyl-β-hydroxybutyric acid, $Me\cdot CHOH\cdot CH(C_5H_{11})\cdot CO_2Et$, a thick oil, which, on distillation, decomposes with elimination of water and formation of α-isoamylcrotonic acid,—

$$MeCH{:}C(C_5H_{11})\cdot CO_2H \text{ (b. p. 240°).}$$

That ring-formation had not taken place in this case was shown by the fact that the acid obtained is unsaturated, and, on oxidation, yields isobutylacetic acid, $C_5H_{11}CO_2H$. When isoamylacetone, $C_5H_{11}\cdot CH_2\cdot CO\cdot Me$, is treated with hydrocyanic acid and the product hydrolysed, a small quantity of α hydroxy-β-isoamylisobutyric acid,—

$$C_5H_{11}\cdot CH_2\cdot C(OH)(Me)\cdot CO_2H,$$

is formed, which melts at 66, and is isomeric with the isoamylhydroxybutyric acid mentioned above.

90. "*Methylisoamylsuccinic Acid.*" I. By W. Trevor Lawrence.

The author is preparing methylisoamylsuccinic acid in large quantities, in order to obtain from it, if possible, by oxidation or bromination, and subsequent splitting off of water or hydrogen bromide respectively, an acid possessing the constitution of camphoric acid (see preceding abstract) suggested by Perkin in 1896, and independently in 1897 by Bouveault (*Bull. Soc. Chim.*, 3, xvii., 990); this paper contains only such results as confirm those of Auden, Perkin, and Rose.

When ethyl α-methyl-α'-cyansuccinate, isoamylbromide, and sodium ethylate are heated, in molecular proportions, and the product of the condensation distilled under diminished pressure, ethyl α methyl-α'-cyan-α'-isoamylsuccinate, $CO_2EtC(C_5H_{11})(CN)\cdot CH(Me)CO_2Et$, is obtained (b. p. 182°, 30 m.m.), which, on hydrolysis with alcoholic potash, gives, after acidifying, a semi-solid acid mass, probably consisting of the cyansuccinic acid. A similar acid was also prepared as follows:—

Isoamylacetic acid is converted by bromine and phosphorus pentabromide into the acid bromide of α-bromisoamylacetic acid, which, with alcohol, gives ethyl α-bromisoamylacetate, $C_5H_{11}CHBr(CO_2Et)$, (b. p. 146°, 65 m.m.); this condenses with ethyl sodio cyancetate to form ethyl α-cyan-α'-isoamylsuccinate (b. p. 196°, 35 m.m.).

Ethyl α-cyan-α'-isoamylsuccinate,—

$$CO_2Et\cdot CH(CN)\cdot CH(C_5H_{11})(CO_2Et),$$

is converted into isoamylsuccinic acid,—

$$(CO_2H)\cdot CH_2\cdot CH(C_5H_{11})CO_2H,$$

(m.p. 76°), on hydrolysis, and is identical with the acid obtained by Fittig and Schirmacher (*Annalen*, 1898, ccciv., 295); on treatment with methyl iodide and sodium ethylate, it is converted into ethyl α-cyan-α-methyl-α'-isoamylsuccinate, $CO_2Et\cdot C(CN)(Me)\cdot CH(C_5H_{11})CO_2Et$, b.p. 185°, 30 m.m.), which, on hydrolysis, gives a similar cyansuccinic acid to the one mentioned above.

Both of these cyan-acids give, on hydrolysis, a mixture of *trans*- and *cis*-methylisoamylsuccinic acids,—

$$CO_2H\cdot CH(Me)\cdot CH(C_5H_{11})(CO_2H),$$

which may be separated either by distillation in a current of steam, in which the *cis*-acid is volatile, or by means of ligroin, in which the *trans*-acid is insoluble.

trans-Methylisoamylsuccinic acid crystallises from benzene or hot water in prisms (m. p. 141—142°), and is converted by acetyl chloride into the anhydride (b. p. 170°, 25 m.m.).

cis-Methylisoamylsuccinic acid is not easily re-crystallised; it is obtained from the pure anhydride as a crystalline powder (m. p. 93°); the anhydride is obtained as an oil (b. p. 187°, 50 m.m.) by the action of acetyl chloride. The anil melts at 116°.

This anhydride, heated with bromine and chloroform in a sealed tube for ten hours is converted into β-isoamylcitraconic anhydride,—

$$\begin{matrix} C_5H_{11}C\!-\!CO \\ \| \qquad\quad \end{matrix}\!\!>\!O, \text{ an oil (b. p. 170°, 50 m.m.);}$$
$$MeC\!-\!CO$$

the free acid does not appear to exist.

On treatment with aniline, the anhydride, which reduces permanganate in the cold, is converted into the characteric anil, which crystallises from methyl alcohol in needles, (m. p. 71°).

(To be continued).

Sulphate of Ammonia.—The prize of 500 guineas, offered by the Sulphate of Ammonia Committee for the best essay on "The Utility of Sulphate of Ammonia in Agriculture," has been awarded by the judges—Mr. J. Bowen-Jones, of Shrewsbury, and Dr. J. Augustus Voelcker, of London—to Mr. James Muir, M.R.A.C., formerly professor at the Royal Agricultural College, Cirencester; subsequently at the Yorkshire College, Leeds; now County Instructor in Agriculture to the Somerset County Council. Seventy-three essays were sent in.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 23, June 5, 1899.

Molecular Refraction, Molecular Dispersion, and Specific Rotatory Power of Compounds of Camphor with Aromatic Aldehydes.—A. Haller and P. Th. Muller.—The authors have determined the above indices for the compound benzylidene camphor and its analogues, with respect to the sodium line and the three rays of hydrogen, α, β, and γ, at a temperature $20° \pm 0·2$ with Pulfrich's refractometer. The same constants were also calculated theoretically for the same rays. It was found that the addition of aldehydes to camphor has the effect not only of increasing the refraction and molecular dispersion, but also of considerably increasing the rotatory power of the molecules.

Use of Chlorate of Potash in Nitrate of Ammonium Explosives.—H. Le Chatelier.—Nitrate of ammonium explosives have come into general use in mines, but many accidents have occurred through admixtures of chlorate of potash. The author investigates the action of these two substances on one another, and finds that in reality an isomorphous mixture is formed of the two salts. The two salts are dissolved in a sufficient quantity of water to keep them in solution at the ordinary temperature. On cooling a small quantity of crystals is deposited, which can be examined.

Effect of Low Temperatures on certain kinds of Steel.—F. Osmond.—The author examines the properties of a series of nickel steels; finding that, if non-magnetic to start with, after immersion in liquid air for five minutes, magnetic properties are acquired. If the greater part of the nickel is replaced by manganese, the same is true. If these two metals are replaced by carbon (1·4 to 1·6 per cent of carbon by preference), and the steel, being heated to about 1050°, is plunged into iced water, two structural constituents are formed,—one hard, as normal steel, the other relatively soft, like manganese or nickel steels. After some moments' immersion in liquid air, the metal, on being brought back to ordinary temperature, is found to be profoundly modified. Its magnetic permeability and its permanent magnetism are increased; its density is decreased from 7·798 to 7·692. If one face was originally polished, the polish disappears. The explanation of these facts appears to be that the lowering of the point of allotropic transformation of iron is comparable with the lowering of the solidification-points of the solvents by the substances dissolved.

Action of Phosphoretted Hydrogen on Copper, Copper Suboxide, and Ammoniacal Salts of Copper.—E. Rubénovich.—In a previous paper the author described the result of his researches on the action of hydrogen-phosphide on an aqueous solution of copper sulphate. The same method is now applied to the investigation of the action of this gas on other compounds of copper. On copper itself the gas appears to have the following action: $PH_3+3Cu=PCu_3+1·5H_2$. The copper phosphide formed slowly oxidises in an atmosphere of oxygen towards 100° with incandescence. On copper suboxide the reaction is represented by the equation—

$$3Cu_2O+2PH_3=2PCu_3+3H_2O,$$

the copper phosphide having the same properties as that formed as above. Hydrogen phosphide has no action on an ammoniacal solution of copper chloride. On the sulphate solution a phosphide, P_2Cu_5,H_2O, is formed, the proportion of the constituents being—

$$\frac{CuSO_4}{PH_3}=2.$$

With solutions of the formate and acetate of copper an oxidised compound, Cu_3PO, is formed, the proportion being

$$\frac{Salt}{PH_3}=2·5, \text{ \&c.}$$

Aloïns.—E. Léger.—The author prepares and investigates the properties of two crystalline substances obtained from Natal aloes. Nataloïn, which has already been prepared, and another aloïn, differing from nataloïn in having one group less of CH_2, and for this reason called homonataloïn. The following reactions enable these two aloïns to be distinguished from barlaloïn:—(1.) A solution of the substance, containing sulphuric acid, to which is added a grain of manganese dioxide or bichromate of potassium, turns a bright green colour. (2.) If a grain of ammonium persulphate is added to the sodium solution, a violet colour appears little by little.

Some Derivatives of Disymmetric Tetramethyl-diamidodiphenylethane. — A. Trillat. — Already inserted.

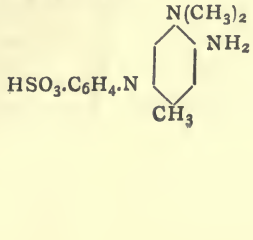
Some Colour Reactions of Oxycellulose. — Edm. Jandrier. — Oxycelluloses, particularly that obtained by the oxidation of cotton by means of potassium chlorate, by Leo Vignon's method, give, in a similar manner to all bodies of the aldehyde formation, colour reactions when treated with sulphuric acid in presence of a phenol.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., October 24, 1898.

Remarks on the Action of Acetylene on Nitrate of Mercury.—P. Köthner.—Basing his opinion on a series of analyses, the author has come to the conclusion that a product is formed by this reaction having the composition $C_2Hg_3NO_4H_2$, which he considers to be a nitrate of the carbide of mercury, $HgC\equiv C.Hg+HgNO_3+H_2O$; K. H. Hofmann arrived at a different conclusion. He now proposes to try and find out the cause of this difference, which may possibly be due to a difference in the conditions under which the experiments are carried out. The ease with which the above compound gives off aldehyde has led to a synthetic method for the production of acetaldehyd by means of acetylene.

Naphthopicric Acid.—F. Kehrmann and W. Haberkant.—The authors have examined the raw product from the nitration of Martius yellow (dinitro-α-naphthol, $OH.NO_2NO_2$-1 : 2 : 4; besides the trinitro-α-naphthol already known, they have obtained by fractional crystallisation an isomer fusible at 145°. This latter, by oxidation with dilute nitric acid, gives 1 : 2 : 4-nitrophthalic acid, in which the third nitro-group ought to be found in one of the β positions of the second nucleus. The authors have, by means of Diehl and Merz's naphthopicric acid, prepared diaminonaphthoquinone-imide; they found that this latter body, when heated in aqueous acid solution, is easily transformed into a mixture of diaminonaphthoquinone and aminonaphthoquinone, while the expected oxynaphthoquinone-imidic derivative was not found.

Contributions to the Rules of Substitution in the Formation of Azoic Colouring-matters. — J. Pinnow and A. Matcowich. — One of the authors recently announced that *m*-amido-dimethyl-*p*-toluidine gives, with sulphonic dinitrobenzene, an azoic colouring-matter, the constitution of which was not established. The authors are now able to state that the azoic group is in the para-position with regard to the amido group, and that consequently the group "dimethyl-amido" is not opposed specially to the azoic group. The constitution of this colouring-matter is therefore—



The Transformation of Nicotic Acid into β-Amidopyridine.—Th. Curtius and E. Mohr.—By heating the ether of nicotic acid with hydrate of hydrazine, we obtain nicotic hydrazide, $C_5H_4N.CO.NH.NH_2$, fusible at 158—159°, of which the chlorhydrate crystallises in white needles fusible at 227°: this hydrazide, when shaken up in aqueous solution with benzaldehyde, gives the hydrazide of benzalnicotic acid. When we add to a solution of hydrochlorate of nicotic hydrazide, a cold solution of two molecules of nitrite of sodium, and keep stirring and cooling, nicotic azide is formed; the ethereal solution of this azide, when digested with absolute alcohol until no more nitrogen comes off, gives β-pyridylurethane: if this latter body is digested with fuming HCl until no more carbonic acid comes off, the already-known hydrochlorate of β-amidopyridine is formed, $C_5H_4NNH_2+2HCl$, melting at 173·5—174·5°.

On β-Diazopyridine and β-Diamidopyridine.—A. Mohr.—The author has dinitrated the hydrochlorate of β-amidopyridine, and joined it in alcoholic solution with resorcine, thus obtaining pyrodine-nitro-resorcine, $C_5H_4N.N=NC_6H_3(OH)_2$, a colouring-matter which dyes wool and silk a yellowish brown in an acid or alkaline bath. In the pure state it occurs in prisms fusible at 218°. He also describes β-dinitro-amidopyridine, obtained by reacting with 1 molecule of nitrite of sodium on 2 molecules of hydrochlorate of β-amidopyridine. The solutions of dinitropyridine appear to decompose, even in the cold, when an attempt is made to reduce them by $SnCl_2+HCl$. The reduction of dinitro-sulphonic acid by zinc powder and acetic acid is much sharper; a solution of pyridylhydrazine is obtained, which, when shaken up with benzaldehyde, gives benzal-β-pyridylhydrazine in needles fusing at 163—164°.

On the Hydrazines and the Azoïc Compounds of the Pyridine Series.—W. Marckwald.—The author has already observed that the amido-group, α or γ, in pyridine prevents the dinitration, inasmuch as the dinitric derivatives decompose immediately on being formed; β-amidopyridine alone is able to give dinitric compounds. The author has attempted to prepare the hydrazines, starting from the α and γ chloropyridines; it is well known that these derivatives are transformed by ammonia into amidopyridines. While ammonia acts above 200°, hydrazine transforms the compounds, even quantitatively, in the desired manner at 150°.

MISCELLANEOUS.

Society of Arts.—The Albert Medal for the present year has been awarded by the President and Council to Sir William Crookes, F.R.S., for his extensive and laborious researches in chemistry and in physics, researches which have, in many instances, developed into useful practical applications in the Arts and Manufactures. Sir William Crookes was among the first to employ the spectroscope as an instrument of chemical research, and by its aid, in 1861, he discovered the metal thallium, the earliest of the series of the "rare metals." To his researches was also due the discovery of the various earths now so extensively employed in obtaining a large increase of light from illuminants. In 1872, he began the long series of experiments on radiation, of which the radiometer was the first outcome. This work on molecular physics in high vacua led to methods of producing extremely high vacua, which made possible the construction of the incandescent lamp. They also enabled the remarkable properties of the cathode rays (which are affording such important results in connection with surgery) to be discovered and developed. He has rendered important services to industrial chemistry, and long ago established a position as an authority on the chemistry of dyeing and calico printing. His work in connection with the chemistry of agriculture also requires to be noted. His services to pure science have been acknowledged by the award of a Royal Medal, and of the Davy Medal of the Royal Society; and it is the application of these researches to industrial uses which led the Council of the Society to submit his name to the President for the award of the Albert Medal.—*Journal of the Society of Arts*, June 30, 1899.

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THE PARENT-ROCK OF THE DIAMOND IN SOUTH AFRICA.*

By Professor T. G. BONNEY, D.Sc., LL.D., V.P.R.S.

(Concluded from p. 6).

Eclogite Boulders without Diamonds.

3. Part of a boulder, which must have been about a foot in diameter.—In macroscopic aspect it presents a general resemblance to the rocks described above, with, however, the possibility of a second green constituent. This is not confirmed on microscopic examination. The rock consists, practically, of pyrope and diopside, as already described, except that negative crystals are rather unusually conspicuous in the latter. Into the details of these, as the point seems not to have any bearing on the present investigation, I do not purpose to enter.

4. A fragment, more irregular in form than the others, measures, very roughly, about 7 in. by 4¾ in. by 3½ in. It retains a good piece of the outer surface, which, though now a little corroded, was once smooth. The rock, which is rather decomposed and crumbly, consists chiefly of three minerals: garnet, not quite so large, paler and more pink in colour than the last-named; an emerald-green pyroxene, and a yellowish or greenish grey, platy to fibrous mineral, suggestive of a second more altered pyroxene. In thin slices the paler and pinker tint of the garnet is very perceptible, as well as the tendency to a rude and generally parallel cleavage. But we find in it, under the microscope, a few microlithic enclosures, of an apparently colourless mineral, which occurs in long prisms crossed at about 70° by an occasional transverse cleavage, and extinguishing at an angle of about 26° with the longer edge. Many of the cracks exhibit slight decomposition, starting from them, and are sometimes occupied by calcite. The pyroxene, under the microscope, hardly differs from the one already described, except that the green tint is slightly richer and one or two crystals contain the small dark brown negative crystals, common in hypersthene and diallage. The dominant cleavage, as before, is along the clinopinacoïd.†

The third mineral proves to be an altered enstatite, but I leave the details for the present as it is better preserved in another rock. A fourth constituent is also present, but more sparingly, viz., a pale brown mica, only moderately pleochroic (phlogophite ?). It occurs generally in plates, averaging about 0·1 inch long. The minerals appear to have formed in the following order: (*a*) garnet, (*b*) diopside, (*c*) mica, (*d*) enstatite. As before, iron oxides are very inconspicuous; there may be a grain or two (small) of serpentinised olivine. The marked presence of enstatite distinguishes this rock from the others, but it differs from the eulysites by the substitution of that mineral for olivine, and so links those rocks to the more ordinary eclogites. The occurrence of a little mica indicates the presence of a small amount of an alkali in the magma. If necessary we may name it newlandite, but personally I should prefer to call it an enstatite-eclogite, for I think the coinage of fresh titles more often a bane than a boon to science.

5. This boulder is almost perfect, except that the general flatness of one side indicates either traces of an old fracture or considerable loss by crumbling. The surface has been smooth, but it has suffered from unequal weathering of the minerals. Its girth, in three directions at right angles, is approximately 20¼ in. by 19½ in. by 17½ in. It appears only to differ from the last-described in having its garnets a shade more purple, and in an approach to a banded structure; the diopside being rather more abundant in a middle zone, the garnet in one, the enstatite in the other of the outer zones. Being satisfied that it is merely a variety of the last-described rock, I have preferred to leave it as an intact boulder.

6. The next fragment, measuring about 3 in. by 2½ in. by 2 in. and retaining part of its smooth outer surface, is labelled "Found in the yellow ground of No. 2 mine,* 50 feet deep." Though it is much more decomposed than the others, the purplish garnet, the emerald-green pyroxene, the altered enstatite (here very rotten), and a flake or two of phlogophite (?) are easily made out. It is obviously a more decomposed specimen of the rock represented by the two preceding specimens.

7. The last of this group of specimens is a rock fragment,† measuring about 3½ in. by 2 in. in length and breadth, and slightly exceeding an inch in greatest thickness. Its outline is irregular, being determined by the fracture of the predominant diallage-like mineral. The crystals of this run large, an inch or more in length, breadth, and thickness. It is greyish-green in colour, having one dominant cleavage, with a sub-metallic lustre, and close subordinate cleavages, giving a somewhat fibrous aspect to that surface. Between these large crystalline lumps, numerous small, ill-defined garnets (pyrope) seem crowded, so as to form fairly continuous partings, generally hardly 0·1 inch in thickness. As the readiness with which the rather soft pyroxenic constituent split away made it improbable that a good slice could be cut, and I was reluctant to injure the specimen, I contented myself with detaching a few flakes of this constituent for microscopic work, since the determination of its identity was sufficient for my purpose. These show the mineral to have one easy cleavage and a rather fibrous structure; they give straight extinction parallel with this. As the usual rings and brushes can be seen on the face of easy cleavage, the mineral belongs to the bastite group. The same is true of the enstatite in boulder (4), though, as it is slightly more fibrous, and not in quite so good a condition, the optical picture is less distinct. Thus we may name the rock from which the present specimen has been broken, a garnet-bearing bastitite.

8. This specimen, said to be a fragment of a boulder, is very different from the rest. It is a compact greenish grey rock containing enclosures, which give it the aspect, at first sight, of a pebbly mudstone. Microscopic examination shows it to be a compact felspathic diabase, with vesicles, which have been filled up with calcite, chlorites, and other secondary minerals (probably zeolites), but not to have any special interest. Its relations appear to be with the rocks occurring in a conglomerate which we shall mention in a later paragraph.

The "Blue Ground" and Associated Rocks.

Two areas of diamantiferous rock are now being worked at the Newlands Mines. The shape of the one which supplied most of the specimens described in this paper is irregular, and, so far as I know, exceptional. Its outline at the surface may be roughly compared to a rounded triangle into the base of which the point of a rather short shuttle is thrust, the greatest breadth of the two being about equal. Exploratory workings at a depth of 300 feet show that the former area rather quickly narrows, and the latter terminates in clefts; the "blue ground," in fact, appears to fill a fissure, broadening in two places to vents which have been traced for some distance underground southwards from the principal mass of

* A Paper read before the Royal Society, June 1, 1899.

† As noticed by Professor Lewis, *ut supra*, p. 22, in the diopside, the prism cleavage has practically disappeared, and a clinopinacoïdal cleavage replaces the orthopinacoïdal usual in diallage.

* The others come from another mine (No. 1).

† I am informed that this was not part of a boulder, but came out of the "blue ground" nearly in its present condition.

diamantiferous rock, as represented in the annexed section.

An igneous rock occurs on either side. It is compact, a greenish grey in colour, not unlike some of the less acid Welsh felstones. Under the microscope it is found to be much affected by secondary mineral changes: the iron oxides alone being in good preservation. A few small crystals of decomposed felspar are scattered in a yet more decomposed matrix, of which the minor details are uninteresting. The rock may be classed with the compact, rather felspathic, diabases. These, farther to the south, turn off rather sharply to east and west.

In the interval, about 12 feet in width, between walls of this diabase, ribs of the "blue" and a mudstone alternate, the thickest one of the former being from 3 to 4 feet in width, and the inner part of it is in better preservation than the outer. Specimens have been examined from the heart of the mass (vii), a part outside it (vi), and the exterior portion (v). The first (vii) in texture, hardness, and colour, reminds me a little of the dark serpentine found north of Cadgwith, in Cornwall. In this matrix roundish spots occur, some darker than it, others a yellow-green colour, besides a few angular whitish spots. The block is traversed by two or three thin calcareous veins. Specimen (vi), while generally similar, is more decomposed, and apparently contains some fragments of the interior (on the whole the best preserved rock) it is locally assuming a green colour, no doubt by hydration. In the specimens from the thick rib, the one last named contains mineral grains and rock fragments, except for a few flakes of the usual mica. The former are a mixture of two fibrous minerals, the larger part corresponding with actinolite; the rest, giving lower polarisation tints, may be serpentine. This fact, and structures suggestive of the former presence of a cleavage more regular than that of olivine, make it more probable that diopside was the original mineral. Though iron oxide is present in specks and rods (especially in the worst preserved specimen), this occurs either in the outer part, or as though it had been deposited along cleavage planes. In the thin rib of "blue" (iii) some of the grains are composed partly of a fibrous mineral, as above described, and partly of a clear one, which often affords rather rich polarisation tints, and presents some resemblance to quartz. Its precise nature is difficult to determine, owing to the absence of distinctive characters, but I believe it to be of secondary origin. Rock fragments are not common in the first (interior) specimen (vii); one, however, is probably an altered shale, and another possibly a limestone. This is bordered by a pale pyroxenic mineral piercing into the grains of calcite. In the second specimen (vi) fragments are rather common; among them are those of diabase,

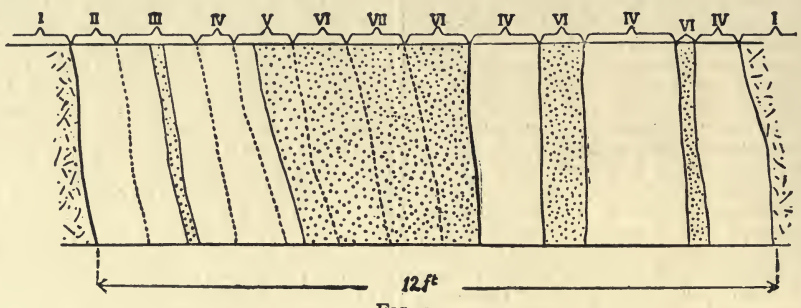


FIG. 3.

shale. Specimen (v) has a stratified aspect, being a dull grey faintly mottled rock, with streaky, dark, rather carbonaceous-looking bands; the origin being doubtful, till it is seen under the microscope. A fourth specimen (iii) shows the mudstone traversed by a vein of rather pale-coloured decomposed "blue," not exceeding an inch in thickness. A fifth (ii) is from near the diabase on the western side, a dark compact rock, faintly mottled, here and there presenting a slight resemblance to a "blue" traversed by thin veins of a carbonate; and sixth (iv) from a like position on the opposite side is a generally similar rock, but with wider veins filled with more coarsely crystalline calcite. The last specimen represents the "blue" in the "neck," a few yards to the north and at the same level (300 feet). This, inferior in preservation to the first-named, includes numerous rounded fragments a little darker than the matrix, with others, angular to subangular, some also darker and some lighter than it.

A brief summary of the results of microscopic examination may suffice, as these rocks do not materially differ from specimens obtained in the De Beers mine, of which I have published a full account (*Geol. Mag.*, 1895, p. 492, and 1897, p. 448).

The matrix is a mixture, in slightly variable quantities, of granules of calcite or dolomite, serpentine, pyroxene, and iron oxides, in which occur flakes with fairly idiomorphic outlines of a warm-brown mica, moderately pleochroic, corresponding with that described (*Geol. Mag.*, 1897, pp. 450, 451) in one or two specimens from De Beers Mine. The prisms are about 0·002 inch in diameter, and sometimes nearly as thick. This mica, which, as stated in a former paper, I consider a secondary product, occurs abundantly in all the specimens, but in that from ranging from fine to coarse, one specimen of the latter, originally, perhaps, an inch in diameter, showing an ophitic structure; felspar and augite both being rather altered, seemingly by infiltration, and one small fragment resembles a subcrystalline limestone. Specimen (v) does not materially differ, but seems to contain more carbonate than the others. The dark streaking is due to grains of iron oxide or serpentine with much opacite; rock fragments few and small. Specimen (iii) from the thin vein contains a very few small rock fragments, mudstone, or shale, more or less altered, possibly also a compact diabase. The "country rock" is a mudstone, consisting of small chips of quartz and felspar, variable in size, embedded in a dusty matrix, including a carbonate, which is more abundant within about a fiftieth of an inch from the junction. The part is slightly stained, but I was unable to detect any signs of contact metamorphism. Specimens (ii) and (iv) are generally similar, but the former contains some small rounded bits of varieties of diabase, and one may represent a crystalline limestone. The veins are filled with calcite and other secondary products, and are bordered by a very thin film of a brown micaceous mineral, like that described as often permeating the "blue." Both specimens suggest micro-mineralogical changes, such as might be produced by the passage of hot water.

Other specimens of the sedimentary rock in the immediate neighbourhood of the blue have been forwarded to me by Mr. Trubenbach, one, from the adit on the southern side of the section mentioned above, is a grey mudstone, containing a flattish rectangular pebble, of a dark green compact rock. Two others are from No. 2 mine, or about 700 yards to the south-west. One, struck in the shaft at a depth of 200 feet, is a conglomerate,

composed of well-rounded rock fragments, with some scattered grains of quartz. Each of the former is bordered by a zone of a crystalline carbonate (impure calcite), and the interstices are filled, sometimes by a clearer variety of the same, but more often by some minutely granular secondary product. Of the rock fragments, one is a sub-crystalline dolomitic limestone; two, perhaps, are chalcedony; the remainder are igneous; the majority being varieties of diabase, sometimes rather decomposed; the rest trachytes, mainly andesites. Their general aspect and the not unfrequent presence of vesicles (now filled with viridite) suggests that they have been furnished by lava-flows. Another specimen, obtained in the same working at a depth of 400 feet, is a rather felspathic diabase, not unlike one of the varieties in the conglomerate. It is a good deal decomposed, is not improbably from a lava-flow, but does not call for a minute description.

Conclusion.

Thus the diamond has been traced up to an igneous rock. The "blue ground" is not the birthplace either of it or of the garnets, pyroxenes, olivine, and other minerals, more or less fragmental, which it incorporates. The diamond is a constituent of the eclogite, just as much as a zircon may be a constituent of a granite or a syenite. Its regular form suggests not only that it was the first mineral to crystallise in the magma, but also a further possibility. Though the occurrence of diamonds in rocks with a high percentage of silica (itacolumite, granite, &c.) has been asserted, the statement needs corroboration. This form of crystallised carbon hitherto has been found only in meteoric iron (Canyon Diablo), and has been produced artificially by Moissan and others with the same metal as matrix. But in eclogite the silica percentage is at least as high as in dolerite; hence it is difficult to understand how so small an amount of carbon escaped oxidation. I had always expected that a peridotite (as supposed by Professor Lewis), if not a material yet more basic, would prove to be the birth-place of the diamond. Can it possibly be a derivative mineral, even in the eclogite? Had it already crystallised out of a more basic magma,* which, however, was still molten, when one more acid was injected, and the mixture became such as to form eclogite? But I content myself with indicating a difficulty, and suggesting a possibility; the fact itself is indisputable: that the diamond occurs, though rather sporadically, as a constituent of an eclogite, which rock, according to the ordinary rules of inference, must be regarded as its birth-place.

This discovery closes another controversy, viz, that concerning the nature of the "Hard blue" of the miners (Kimberlite of Professor Lewis), in which the diamond is usually found. The boulders described in this paper are truly water worn. The idea that they have been rounded by a sort of "cup and ball" game played by a volcano may be dismissed as practically impossible. Any such process would take a long time, but the absence of true scoria implies that the explosive phase was a brief one. They resemble stones which have travelled for several miles down a mountain torrent, and must have been derived from a coarse conglomerate, manufactured by either a strong stream or the waves of a sea from fragments obtained from more ancient crystalline rocks.† The "washings,"‡ a parcel of which I received from Mr. Trubenbach, also show that the boulders are really water worn. Besides two unworn pieces of pyrite and a rough bit of eclogite, about three-quarters of an inch in diameter, the pyroxenic constituent of which was a bright emerald green (? smaragdite), I find part of a subangular fragment of chrome-diopside associated with two or three flakes of the usual mica, a well rounded garnet fully 0·6 inch across, and half a well worn pebble of eclogite, about one inch long and half an inch thick. The rounded water-worn look of the great majority of the smaller constituents (chiefly garnets and pyroxenes), about the size of hemp seed, is very obvious. I had suspected some of the grains washings from the De Beers Mines to have been similarly treated; but here it is indubitable, indeed many of the dark green specimens are so smooth outside that they could only be identified after fracture. The ordinary diopside can, however, be recognised, with some of a clearer and brighter green. Most of the garnets are pyropes, but a few resemble essonite. I find also some grains of iron oxide and of vein quartz. Thus, the presence of water-worn fragments, large and small, in considerable abundance, shows the "blue ground" to be a true breccia, produced by the destruction of various rocks (some of them crystalline, others sedimentary, but occasionally including water-worn boulders of the former)—*i.e.*, a result of shattering explosions, followed by solfataric action. Hence the name Kimberlite must disappear from the list of the peridotites, and even from petrological literature, unless it be retained for this remarkable type of breccia.

Boulders, such as we have described, might be expected to occur at the base of the sedimentary series, in proximity to a crystalline floor. The Karoo beds in South Africa, as is well known, are underlain in many places by a coarse conglomerate of considerable thickness and great extent, called the Dwyka conglomerate, which is supposed to be Permian or Permo-carboniferous in age. It crops out from beneath the Karoo beds at no great distance from the diamond-bearing district, and very probably extends beneath it. If this deposit has supplied the boulders, the date of the genesis of the diamond is carried back, at the very least, to Palæozoic ages, and possibly to a still earlier era in the earth's history.

* This, however, cannot have been very rich in iron, because diopside does not contain much of that constituent.

† As these eclogites are very coarsely crystalline, we are justified in assuming they were once deep-seated rocks, and so much more ancient than the date of the conglomerate. To prevent any misunderstanding I may repeat that the matrix from which these boulders were taken (at various depths, from nearly 100 to about 300 feet) cannot be any alluvial deposit, but is the typical "blue ground," practically identical with that in the Kimberley mines.

‡ The name is given to the mineral residue left after washing away the decomposed matrix of the "blue ground."

NOTE ON THE ACTION OF LIQUID HYDRIODIC ACID ON ETHYL ETHER.*

By F. G. COTTRELL and ROY RAVONE ROGERS.

SOME time ago, while examining the properties of liquid hydriodic acid (Norris and Cottrell, *Am. Chem. Journ.*, 1896, xviii., 103), it was noted that when the acid was mixed with ether a vigorous action occurred, the temperature rising rapidly, the mixture, which at first appeared to be homogeneous, separated into two layers, one of which was assumed to be ethyl iodide, judging from its appearance and odour, and the other was assumed to be water and the excess of acid. No attempt was made at the time to separate and purify the product, or to determine the yield. The following supplements the previous work in this particular.

The hydriodic acid was prepared and dried according to the method described in the previous paper (*loc. cit.*). The ether was prepared by washing commercial ether with a considerable volume of water, digesting with quicklime for a few days, and distilling from the same. This was again distilled, and then gave a boiling-point constant within a tenth of a degree.

After several preliminary experiments the following form of apparatus was adopted. We believe it will be found a very convenient form for reactions which are to be carried out under pressure.

The sealed end of a straight eudiometer-tube provided

* Contributions from the Chemical Laboratory of the University of California. From the *American Chemical Journal*, xxi., No. 1.

with a glass stop-cock was cut off, and a smaller tube, sealed at one end, introduced into it, open end first. The cut end of the large tube was then sealed, thus providing a vessel of two chambers, into each of which liquids could be introduced through the stop-cock.

The whole apparatus was now weighed, the tube was then surrounded with solid carbon dioxide, and gaseous hydriodic acid conducted by means of a narrow delivery-tube to the bottom of the eudiometer-tube, where it condensed to a liquid surrounding the inner tube. When about 15 c.c. of this liquid had been collected, the delivery tube was withdrawn, and the acid cooled until it solidified. Then a weighed amouut of ether was run into the inner tube, and the stop-cock closed, and tied in securely.

The apparatus was now tipped slightly so that the ether mixed in small quantities at a time with the acid. The ether on coming in contact with the solid acid produced a vigorous reaction. The latter melted rapidly, even while surrounded by the solid carbon dioxide. If the ether and acid are suddenly mixed the temperature will rise from the freezing-point of the acid (−55° C.) to at least +40° or 50°. When mixing was complete the whole apparatus was weighed to determine the weight of acid used.

During the mixing the products began to separate into two layers. The tube was set aside for a week in a dark place (average temperature about 18°), at the end of which time the heavier of the two layers had relatively increased in volume. After being cooled down somewhat, the tube was opened. Water was added, which mixed with the upper layer, but would not mix with the lower. The lower layer was washed with water, then with a little weak solution of caustic potash, dried over calcium chloride, and distilled twice. The following are the numerical data:—

	Grms.
Weight of ether used..	8·91
Weight of acid used	42·30

This is 1·33 times the quantity of acid required by theory for the reaction $(C_2H_5)_2O+2HI=2C_2H_5I+H_2O$.

Weight of crude product after washing with water, 35 grms.; this is 94 per cent of the quantity required by theory.

Weight of product after first distillation, 32·8 grms., which is 88 per cent of the quantity required by theory.

After the second distillation the whole of the material boiled between 71·9° and 72° under 756 m.m. pressure. The boiling-point of ethyl iodide, given by different authorities (Landolt and Börnstein, *Chem. Phys. Tab.*, 1894, p. 65), ranges about a degree on each side of this. Its specific gravity at 18° referred to water at the same temperature was found to be 1·941. Hagen gives 1·935 at 20°, and Linnemann 1·944 at 14·5° (*loc. cit.*). Its refractive index for the D line was 1·5133 at 18·5°. Hagen (*loc. cit.*, p. 427), gives 1·5131 at 20°.

Silva (*Compt. Rend.*, 1875, lxxxi., 323), found that when gaseous hydriodic acid reacted on methyl ether at 0° to 4°, the whole of the ether was converted into methyl iodide. With ethyl ether, on the contrary, only part was converted into iodide and part into alcohol; and the same was true for the higher ethers. No quantitative data are given.

The formation of water by the reaction itself in such cases as the above, soon establishes the same condition as when using a concentrated aqueous solution of the acid. It would be interesting to study the behaviour of the anhydrous acid in reactions where no water can form; *e.g.*, in the addition of hydrogen to benzene (*Cf.* Berthelot, *Journ. Prakt. Chem.*, 1868, civ., 106).

It seems not improbable from the rapid and widespread increase in our facilities for liquefying and handling considerable quantities of gases that this method of applying such reagents as chlorine, sulphur dioxide, and ammonia may eventually come into quite general use. It has the great advantage of permitting a high concentration of the reagent without the necessity of introducing water or other solvents, while its practical application is by no means as difficult as might at first be supposed.

THE ELECTROLYTIC SEPARATION OF CADMIUM FROM IRON.

By W. STORTENBECKER.

A METHOD for separating these two metals in slightly acid solution has already been described by Smith. As a cyanide solution gives the best deposits of cadmium the author has made certain experiments with the object of finding out whether such a solution could not be used for the electrolytic separation of iron from cadmium.

When an excess of cyanide of potassium is added to a solution of a ferrous salt, a soluble ferrocyanide of potassium is formed. With solutions of ferric salts, hydrated peroxide of iron is produced, and only a very small proportion of iron passes into the cyanide solution.

The method proposed by the author is based on the non-electrolytic decomposition of the soluble ferrocyanide of potassium.

The mixed salts of iron and cadmium are dissolved in 100 c.c. of water very slightly acidulated with a few drops of dilute sulphuric acid; to this is added 2 or 3 grms. of pure cyanide of potassium, and the whole heated until the solution becomes perfectly clear. If this clarification requires too long a time a few drops of caustic potash may be added. The solution is then diluted to 200—250 c.c., and, after cooling, electrolysed with a current of 0·05 to 0·10 ampère per square decimetre. The deposit of cadmium is perfectly coherent.

If the solution contains but a very small quantity of iron, the floating hydrated peroxide may be neglected; but if, on the contrary, the iron is present in any considerable proportion it becomes necessary to reduce this ferric salt to the ferrous state by means of sulphurous acid; to effect this it suffices to add to the acid solution a small quantity of sulphite of soda, and heat for a short while.—*Zeit. für Elektrochem.*, iv. [17], p. 409.

CARNOTITE: A NEW MINERAL.

By MM. FRIEDEL and CUMENGE.

ONE of us has recently received from America several samples of a new uraniferous mineral. It occurs in the form of a yellow powder or mass easily crumbled between the fingers, which it stains strongly yellow. A preliminary examination showed that this mineral is principally formed, in most samples at any rate though we have had purer ones, of silica in the form of sand. This sand is intimately mixed with a yellowish material consisting of very small grains of which it is impossible to identify the structure, even with a very high power microscope, although it is undoubtedly crystalline, and acts on polarised light.

By repeated levigations a great part, though not the whole, of the sand can be removed. For this reason we preferred to analyse the material as it was, after removing the silica by the action of dilute nitric or hydrochloric acid, which easily dissolved the yellow uraniferous substance. By this means we get with nitric acid a yellow solution, and with hydrochloric acid a beautiful green one.

The mineral contains a certain proportion of water, but it is not advisable to calcine at a bright red heat to effect its determination, as it is very difficult to afterwards dissolve it in acid, and the silica remains brown, the colour taken by the mineral itself after calcination.

We have found that the matter dissolved in nitric acid contains, besides a considerable quantity of uranium, both

vanadic acid, iron, aluminium, and traces of copper, lead, and potassium. We also found that it contains, besides the other minerals of vanadium, a certain proportion of the radiant metals discovered by M. and Madame Curie, but these elements are only met with in very small quantities.

The most convenient manner for conducting the analysis consists in evaporating the nitric solution to dryness on the water-bath with an excess of nitric acid, which must be afterwards driven off; after this the residue is taken up with water and filtered. The nitrate of uranium which is undecomposable under these circumstances passes into the filtrate. The vanadic acid, on the contrary, forms with the nitric acid a compound which is destroyed by evaporation, and becomes insoluble in water, especially when nitrate of ammonia is present.

After well washing the filtrate is again evaporated down with nitric acid. After repeating this operation we get, on the one hand, a solution containing the uranium; and on the other hand, on the filter, a precipitate containing the vanadium accompanied by the iron and aluminium.*

The vanadic acid is separated from the iron and aluminium by treating the precipitate on the same filter, placed for this purpose on a funnel fitted with a stop-cock and closed with an indiarubber stopper, with ammonia.

To obtain the vanadic acid it is sufficient to evaporate and calcine the solution of vanadate of ammonia. The iron will be found on the filter in the state of sesquioxide.

Uranium is precipitated in boiling solution by ammonia, and the precipitation repeated a second time, to separate the potash as completely as possible; there now only remains to evaporate the filtrate with the addition of aqua regia, to destroy the ammoniacal salts, then to add sulphuric acid so as to get the potash into the state of sulphate. We can then evaporate the uranic solution to dryness, and take up with alcohol at 95°, which will dissolve the nitrate of uranium, and leave the nitrate of potassium undissolved. Nevertheless, this latter process has not given such good results as the first one.

We have by this means obtained figures leading to the formula $2U_2O_3.V_2O_5\ K_2O.3H_2O$.

This requires:—

U_2O_3	63·54
V_2O_5	20·12
K_2O	10·37
H_2O	5·95
	99·98

We found.—

U_2O_3	64·70	62·46
V_2O_5	20·31	19·95
K_2O	10·95	11·09
Fe_2O_3	0·96	0·65
H_2O	5·19—4·81	5·19—4·81

The proportion of iron is rather variable; we further noticed on different samples that the sesquioxide of iron forms irregularly divided veins. As for the silica it varies as much as from 10 to 60 per cent, and even more. In an exceptional sample there was only 1·3 per cent, and in another only 7·8 per cent. As for the water the amount has not been definitely determined; we began with the simply air-dried mineral, and found that the quantity present was less than that required by the formula.

However that may be, though, it is clear that we have to deal with a new mineral which constitutes a well defined species. We propose to dedicate it to M. Adolphe Carnot, Member of the Institute, Inspector General of Mines, whose works on mineral analysis are so well known, and who has recently ("Nouvelle Méthode d'Analyse Minerale," p. 55), described, for the estimation of vanadium, the precipitation of the acid in the form of a vanadate of uranium, the formula of which has some analogy with that of the compound we have just described.

This mineral was discovered by M. Charles Poulot, a French chemist, at present living at Denver, in Colorado. He happened to be in the county of Montrose (Colorado), in one of the cavities or pools in the grit-stone rock, which is accompanied by chessylite and malachite. From this source about 10 tons of the mineral was extracted. M. Poulot there recognised the presence of vanadium.

As to the radioactive minerals contained in carnotite, we here give the results found by M. and Madame P. Curie, with their permission.

A sample containing 54 per cent of silica had an activity of 1·25; another much purer and hardly containing any silica, 2·6. The insoluble sulphates mixed with barium and radium, 35; the raw sulphides, 11; finally the sulphides of bismuth and polonium from 50 to 60; the quantity was so small that the results were very uncertain. The activity of uranium was taken as unity.—*Bull. Soc. Chim.*, Series 3, xxi., No. 7.

* A slight difficulty occurs when we want to transfer the vanadic acid to the filter. A small portion remains obstinately attached to the porcelain crucible, and we are obliged to re-dissolve it in dilute nitric acid, and evaporate again to dryness. After two or three similar operations we can eventually get practically all the vanadic acid collected on the filter.

ON THE HYDROSULPHITES OF AMMONIUM.

By MAURICE PRUD'HOMME.

THE treatment of bisulphite of soda by zinc according to Schützenberger's method, gives rise to the formation of acid hydrosulphite of sodium according to the equation, $3SO_3NaH+Zn=SO_2NaH+SO_3Na_2+SO_3Zn+H_2O$. Of the three molecules of bisulphite present, one only is transformed into hydrosulphite.

Neutral Hydrosulphite of Ammonium.—This can be obtained directly by treating the neutral sulphite of ammonium with zinc.

Like the ammoniacal salts in general this sulphite is transformed in the presence of zinc, into a double salt of zinc and ammonium, with the disengagement of hydrogen, $SO_3(NH_4)_2+Zn=SO_3Zn.2NH_3+H_2$. The nascent hydrogen, reacting on a second molecule of the sulphite, converts it into hydrosulphite $SO_3(NH_4)_2+H_2=SO_2(NH_4)_2+H_2O$.

Practically we start with commercial bisulphite of ammonium at 28° B., which must be saturated with NH_3 (100 bisulphite, 20 to 25 ammonia). After cooling we fill with it a flask containing zinc turnings. The flask, properly corked, is alternately shaken to renew the surfaces of contact, and cooled in a current of water. At the end of about ten minutes the reaction is finished. An abundant white deposit of the double sulphite of zinc and ammonium is formed. It is allowed to stand another quarter of an hour, and then filtered. Under these conditions of concentration the filtrate does not contain any zinc.

When treated with permanganate of potash, acidulated with sulphuric acid, it has practically the same reducing power as the neutral sulphite originally taken. The return is about 96 to 98 per cent of theory.

Of the two molecules of sulphite of ammonium present one has been converted into a double sulphite of zinc and ammonium, and the other into hydrosulphite of ammonium.

From the laboratory point of view, this process has the following advantages over that with bisulphite of soda.

1. Greater stability and greater concentration of the product.

2. Easy purification by simple filtrations. (In the bisulphite of soda process the sulphates of Na and Zn must be removed by lime).

3. Hydrosulphite of ammonium is very suitable for the preparation of other hydrosulphites.

This same reaction applied to the hyposulphite, hyposulphate, and trithionate of ammonia has only given negative results.

Acid Hydrosulphite of Ammonium.—When we attempt to prepare the acid hydrosulphite of ammonium by means of bisulphite of ammonium and zinc, we observe the almost immediate formation of a white precipitate, which is not produced in the preparation of the acid hydrosulphite of soda. The explanation of this phenomenon is found in the facts just made known. In a first phase the reaction takes place with the bisulphite of ammonium, as with the sodium—

$$3SO_3H.NH_4+Zn=$$
$$=SO_2H.NH_4+SO_3(NH_4)_2+SO_3Zn+H_2O.$$

The neutral sulphite of ammonia formed, itself enters into the reaction—

$$2SO_3(NH_4)_2+Zn=SO_2(NH_4)_2+SO_3Zn.2NH_3+H_2O,$$

so that, starting with 6 molecules of bisulphite of ammonium, we finally obtain 2 molecules of acid hydrosulphite, 1 molecule of neutral hydrosulphite, 2 molecules of sulphite of zinc, and 1 molecule of double sulphite of zinc and ammonium. The half of the bisulphite is thus again transformed in this case into hydrosulphite.—*Bull. Soc. Chim.*, Series 3, xxi., No 7.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

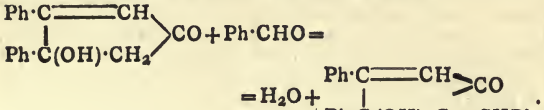
Ordinary Meeting, June 15th, 1899.

Professor T. E. Thorpe, F.R.S., President, in the Chair.

(Continued from p. 10).

91. "*Condensations of Anhydracetonebenzil and its Analogues with Aldehydes.* By Francis R. Japp, F.R.S., and Alexander Findlay, M.A., B.Sc.

The authors find that anhydracetonebenzil (diphenylcyclopentenolone) and benzaldehyde interact in presence of alcoholic potash according to the equation—

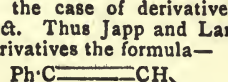


Benzylideneanhydracetonebenzil (m. p. 230°).

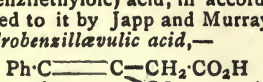
In like manner, by acting on anhydracetonbenzil with cuminaldehyde, they obtained *cumylideneanhydracetonebenzil*, $C_{27}H_{24}O_2$ (m. p. 148°); and with cinnamaldehyde, *cinnamylideneanhydracetonebenzil*, $C_{26}H_{20}O_2$ (m. p. 222°).

By reduction with hydriodic acid, benzylideneanhydracetonebenzil yields a compound $C_{24}H_{18}O$ (m. p. 182°)—probably a *benzylidenediphenylcyclopentenone.*

The authors have applied the interaction with benzaldehyde to determining the constitution of the monosubstitution derivatives of anhydracetonebenzil, in which there is a doubt as to whether the substitution occurs in the CH- or in the CH_2-group. The condensation cannot occur except in the case of derivatives containing the CH_2-group intact. Thus Japp and Lander assigned to the monalkyl derivatives the formula—

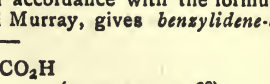


and in accordance with this, it was found that amylanhydracetonebenzil does not interact with benzaldehyde. On the other hand, α-anhydrobenzillævulic (α-anhydracetonebenzilethyloic) acid, in accordance with the formula ascribed to it by Japp and Murray, gives *benzylidene-α-anhydrobenzillævulic acid*,—



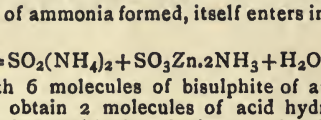
(m. p. 214—216°).

Anhydracetonebenzilcarboxylic acid, however, must have the constitution—



instead of the alternative constitution adopted for it by Japp and Lander, inasmuch as it yields a benzylidene derivative, $C_{25}H_{18}O_4$ (m. p. about 245°).

Anhydracetonebenzil and benzil interact in presence of alcoholic potash to form an aldol condensation compound,—

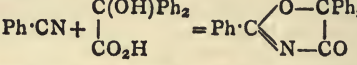


(m. p. 200°),

identical with anhydracetonedibenzil, previously obtained by the condensation of acetone with excess of benzil (*Trans.*, 1885, xlvii., 33). The hitherto unknown constitution of anhydracetonedibenzil is thus ascertained.

92. "*Triphenyloxazolone.*" By Francis R. Japp, F.R.S., and Alexander Findlay, M.A., B.Sc.

By the action of cold concentrated sulphuric acid on a mixture of benzonitrile and benzilic acid, the authors have obtained *triphenyloxazolone* (triphenylketodihydrooxazole),—



It crystallises in large, transparent rhombs melting at 136°. At the same time, *benzimidoxydiphenylacetic acid*, $Ph{\cdot}C(NH){\cdot}O{\cdot}CPh_2{\cdot}CO_2H$, is formed, which is deposited from its solutions in prisms or plates melting at 190°.

Heating with acetic anhydride converts the acid into the oxazolone, whilst boiling with *dilute* potash transforms the oxazolone into a salt of the acid.

When the acid is heated with *strong* potash, it parts with carbon dioxide, and yields *benzimidobenzhydrylic oxide*, $Ph{\cdot}C(NH){\cdot}O{\cdot}CHPh_2$ (needles, m. p. 172—173°). The constitution of the latter compound was proved by its synthesis from benzonitrile and benzhydrol under the influence of gaseous hydrogen chloride. It thus belongs to the class of imido-ethers described by Pinner and Klein (*Ber.*, 1877, x, 1889).

Both the oxazolone and the acid, when boiled for a few minutes with fuming hydriodic acid, yield benzamide and diphenylacetic acid. Under the same conditions, benzimidobenzhydrylic oxide gives diphenylmethane in place of diphenylacetic acid.

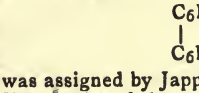
None of the other nitriles and α-hydroxy-acids with which the authors experimented yielded compounds corresponding with the foregoing.

93. "*Interaction of Phenanthraquinone, Acetophenone, and Ammonia.*" By Francis R. Japp, F.R.S., and Andrew N. Meldrum, B.Sc.

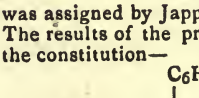
Japp and Streatfeild showed (*Trans.*, 1882, xli, 270) that phenanthraquinone, acetone, and ammonia interact according to the equation—

$$C_{14}H_8O_2+C_3H_6O+NH_3=C_{17}H_{15}NO_2+H_2O,$$

and to the compound thus formed the constitution—



was assigned by Japp and Miller (*Trans.*, 1885, xlvii., 12). The results of the present investigation, however, render the constitution—



analogous to that of diacetonamine, more probable. The compound may be named *acetonylaminophenanthrone*.

Thus the authors find that phenanthraquinone, acetophenone, and alcoholic ammonia interact according to the equation—

$$\begin{matrix} C_6H_4\cdot CO \\ | \quad | \\ C_6H_4\cdot CO \end{matrix} + 2CH_3\cdot CO\cdot Ph + 2NH_3 =$$

$$= \begin{matrix} C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \\ | \quad | \\ C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \end{matrix} + 2H_2O,$$

yielding *diphenacyldiaminodihydrophenanthrene*, which crystallises in colourless, silky needles, and decomposes about 150° without showing a definite melting point. It is evident that a constitution analogous to that ascribed by Japp and Miller to the acetone-ammonia derivative of phenanthraquinone is not possible in the case of this compound.

The acetophenone-ammonia derivative is hydrolysed by aqueous oxalic acid according to the equation—

$$\begin{matrix} C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \\ | \quad | \\ C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \end{matrix} + 2H_2O =$$

$$= \begin{matrix} C_6H_4\cdot C(OH)\cdot CH_2\cdot CO\cdot Ph \\ | \quad | \\ C_6H_4\cdot CO \end{matrix} + CH_3\cdot CO\cdot Ph + 2NH_3,$$

yielding *phenacylhydroxyphenanthrone* (*acetophenone-phenanthraquinone*), which crystallises in small prisms or six-sided plates melting with decomposition at 125—130°.

By the interaction of phenanthraquinone acetophenone, and aqueous ammonia, *phenacylaminophenanthrone*—

$$\begin{matrix} C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \\ | \quad | \\ C_6H_4\cdot CO \end{matrix},$$

analogous to the acetone-ammonia derivative, was obtained. It crystallises in minute, colourless, six-sided plates melting about 160° with decomposition and evolution of gas. A substance, apparently identical with the foregoing, was obtained by the action of the ammonia on phenacylhydroxyphenanthrone.

The ease with which these compounds break up into their generating substances renders a detailed study of their constitution impossible.

Other ketones, such as methyl ethyl ketone and diethyl ketone, appeared to interact in a similar manner with phenanthraquinone and ammonia; but it was found impossible to obtain the resulting compounds in a state of purity.

94. "*Furfuran Derivatives from Benzoin and Phenols.*" By FRANCIS R. JAPP, F.R.S., and ANDREW N. MELDRUM, B.Sc.

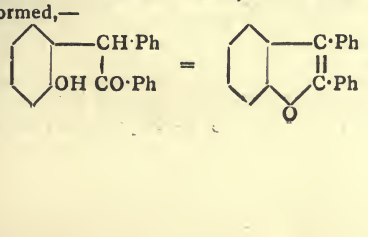
By the action of cold, concentrated sulphuric acid on a mixture of benzoin and phenol, Japp and Wadsworth (*Trans.*, 1890, lviii., 965) obtained paradesylphenolsulphonic acid, from which, by hydrolysing it with strong hydrochloric acid at 150°, paradesylphenol,—

$$\begin{matrix} Ph\cdot CH\cdot C_6H_4\cdot OH \\ | \quad\quad (1:4), \\ Ph\cdot CO \end{matrix}$$

was prepared.

The authors find that, by heating a mixture of benzoin and phenol with sulphuric acid of 73 per cent strength, the foregoing condensation occurs without subsequent sulphonation of the resulting compound, and an excellent yield of paradesylphenol is obtained. The various condensations described in this note were effected by means of a sulphuric acid of this strength.

If the desyl-group were to take up the ortho-position towards the hydroxyl of the phenol, it is evident that, by a further elimination of water, a furfuran derivative might be formed,—

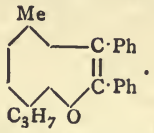


With phenol and benzoin, no such reaction occurs; the para-compound alone is formed. With thymol and benzoin, however, a mixture of desylthymol and cymodiphenylfurfuran is obtained. In the case of resorcinol and of qninol, either one or two diphenylfurfuran groups may be introduced. With phloroglucinol, only the compound containing three such groups was obtafned.

The following compounds have been prepared: (1) From thymol and benzoin. *Desylthymol*,—

$$\begin{matrix} Ph\cdot CH\cdot C_6H_2(Me)(C_3H_7)OH \\ | \\ Ph\cdot CO \end{matrix}$$

Laminæ melting at 126°. The acetyl derivative forms needles melting at 110°. The position of the desyl group in desylthymol is uncertain, except that it is not adjacent to the hydroxyl group. *Cymodiphenylfurfuran*—



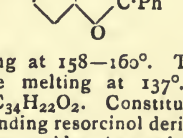
Slender needles melting at 115—116°. (2) From resorcinol and benzoin. *Metahydroxybenzodiphenylfurfuran*,—

$$C_6H_3(OH)\begin{matrix} CPh:C\cdot Ph \\ O\text{——}I \end{matrix}.$$

Slender needles, with satiny lustre, melting at 117·5°. The acetyl derivative crystallises in slender prisms, melting at 117°. The practical coincidence in the melting points of these two substances is anomalous. They differ greatly in their other physical properties. *Metabenzotetraphenyifurfuran*,—

$$C_6H_2\left(\begin{matrix} CPh:C\cdot Ph \\ O\text{——}I \end{matrix}\right)_2.$$

Slender needles, melting at 217—219°. Solutions show a violet fluorescence. Two constitutions, between which it is at present impossible to decide, might be assigned to each of these derivatives. Isomeric forms were not observed. (3) From quinol and benzoin. *Parahydroxybenzodiphenyldifurfuran*,—



Flat needles, melting at 158—160°. The acetyl derivative forms laminæ melting at 137°. *Parabenzotetraphenyldifurfuran*, $C_{34}H_{22}O_2$. Constitution analogous to that of the corresponding resorcinol derivative. Only one of the two possible isomerides observed. Needles melting at 278°. Solutions strongly fluorescent; crystals slightly so. (4) From phloroglucinol and benzoin. *Benzohexaphenyltrifurfuran*,—

$$C_6\left(\begin{matrix} CPh:C\cdot Ph \\ O\text{——}I \end{matrix}\right)_3.$$

Slender needles, melting at 360°.

The foregoing work was completed last year, before the publication of Græbe's investigation of benzoin yellow (*Ber.*, 1898, xxxi., 2975), in which it is shown that, by the action of sulphuric acid on a mixture of benzoin and gallic acid, a compound containing a diphenylfurfuran group is formed.

95. "*Interaction of Benzoin with Phenylenediamines.*" By FRANCIS R. JAPP, F.R.S., and ANDREW N. MELDRUM, B.Sc.

By heating benzoin with aniline and a little aniline hydrochloride, Japp and Murray (*Trans.*, 1894, lxv., 892), obtained 2′ : 3′-diphenylindole. The desylanilide, $Ph\cdot CO\cdot CH(NH\cdot Ph)\cdot Ph$, which is formed in the first instance, parts with water, under the influence of the

hydrochloric acid, yielding the indole. The authors have now studied this reaction with the phenylenediamines, in order, if possible, to obtain the corresponding benzodipyrrhole derivatives. Only in the case of metaphenylenediamine, however, did the reaction take place in the desired sense.

Benzoin, heated with metaphenylenediamine and a little of its hydrochloride, gave *metabenzotetraphenyldipyrrhole*,—

$$C_6H_2\begin{pmatrix}CPh:C\cdot Ph\\ NH-\end{pmatrix}_2,$$

which forms slender needles melting at 282°. Two constitutions are possible for this compound, and at present there is apparently no means of deciding between them. Substituting paraphenylenediamine and its hydrochloride for the meta-compounds in the foregoing reaction *bidesylparaphenylenediamine*, $C_6H_4(NH\cdot CHPh\cdot CO\cdot Ph)_2$, was obtained in the form of bright yellow, minute laminæ melting at 257°. It yields a diacetyl derivative crystallising in slender, colourless needles melting at 279°. By heating either bidesylparaphenylenediamine or its diacetyl derivative with zinc chloride, or by heating benzoin with paraphenylenedianine hydrochloride alone, indications of the formation of a benzodipyrrhole derivative were obtained; but the compound was not formed in quantity sufficient to admit of its purification.

By heating benzoin with orthophenylenediamine hydrochloride, *phenylbenzimidazole*,—

$$C_6H_4\begin{matrix}NH\\ -N\end{matrix}\!>\!C\cdot Ph,$$

was obtained, the benzoin molecule breaking up in the process. Benzoin and free orthophenylenediamine, on the other hand, yielded *diphenylquinoxaline*,—

$$C_6H_4\begin{matrix}N:C\cdot Ph\\ |\\ N:C\cdot Ph\end{matrix},$$

oxidation taking place during the process. The formation of the latter compound in this reaction had, as we afterwards found, been already observed by O. Fischer (*Ber.*, 1891, xxiv., 720).

96. "*The Condensation of Ethyl Salts of Acids of the Acetylene Series with Ketonic Compounds.*" By SIEGFRID RUHEMANN and A. V. CUNNINGTON.

The substitution products of ethyl phenylpropiolate, *e.g.*, ethyl *p*-nitrophenylpropiolate, on treatment with sodium ethoxide, yield, with ethyl acetoacetate and ethyl benzoylacetate respectively, the nitro-substituted cyclic compounds corresponding to the α-pyrone derivatives previously described. The homologues of ethyl acetoacetate, however, on treatment with ethyl phenylpropiolate and sodium ethoxide, give rise to a mixture of compounds which the authors were unable to separate by fractional distillation. The α-pyrone derivatives obtained from β-diketones, like those from ethyl salts of β-ketonic acids, can be transformed into pyridine derivatives. Thus diphenylaceto-α-pyrone yields—

$$PhC\begin{matrix}CH-COH\\ \diagdown\quad\diagup\\ CAc=CPh\end{matrix}\!>\!N \text{ (m. p. 255°).}$$

The intermediate product of this reaction, *i.e.*, the ethyl salt, $CO_2Et\cdot CH:CPh\cdot CAc:CPh(NH_2)$ (m. p. 161—162°), was isolated.

It was further found that ethylamine, like ammonia, yields, with α-pyrone derivatives, additive compounds with two molecules of the amine. The behaviour of ethyl acetylenedicarboxylate differs from that of ethyl phenylpropiolate towards the ethyl salts of benzoylacetic and acetoacetic acids. In these cases, α-pyrone derivatives are not produced, but compounds which are most probably trimethylene derivatives, such as—

$$\begin{matrix}CO_2Et\cdot CH-CH\cdot CO_2Et\\ \diagdown\quad\diagup\\ Bz\cdot C\cdot CO_2Et\end{matrix},$$

a yellow oil with green fluorescence, b. p. 236—237° at 11 m.m., and—

$$\begin{matrix}CO_2Et\cdot CH-CH\cdot CO_2Et\\ \diagdown\quad\diagup\\ Ac\cdot C\cdot CO_2Et\end{matrix},$$

a colourless oil, b. p. 186—187°, at 13 m.m.

97. "*Dextro-ac-tetrahydro-β-naphthylamine.* By WILLIAM JACKSON POPE.

The only amino-derivative of tetrahydronapthalene which has previously been resolved into optically active components is ac-1 : 4'-tetrahydronaphthylenediamine; this base was resolved by Bamberger (*Ber.*, 1890, xxiii., 291) by crystallising its acid tartrates.

On adding a solution of half a molecular proportion of ammonium dextro-α-bromocamphorsulphonate to a hot aqueous solution of synthetic ac-tetrahydro-β-naphthylamine hydrochloride, and allowing to cool, a copious separation of *dextro-ac-tetrahydro β-naphthylamine dextro-α-bromocamphorsulphonate*, $C_{10}H_{11}NH_2,C_{10}H_{14}BrOSO_3H$, occurs; this salt is very sparingly soluble in water, but crystallises from a mixture of alcohol and acetone in long, colourless needles melting at 185—187°, and in a 5 per cent solution in absolute alcohol has the specific rotation $[\alpha]_D = +78°$.

Dextro-ac-tetrahydro-β-naphthylamine,—

$$\begin{matrix}CH\cdot CH:C\cdot CH_2\cdot CH_2\\ ||\quad\quad|\quad\quad|\\ CH\cdot CH:C\cdot CH_2\cdot CH\cdot NH_2\end{matrix},$$

is obtained as a colourless oil on treating its dextrobromocamphorsulphonate with soda, extracting repeatedly with ether, and distilling under reduced pressure. It has the specific rotation $[\alpha]_D = +31°$ at 15° in a 16 per cent solution in benzene. The *dextrocamphorsulphonate*, $C_{10}H_{11}NH_2,C_{10}H_{14}OSO_3H$, obtained by treating the dextrobase by Reychler's dextrocamphorsulphonic acid, separates from aqueous solutions in large, very lustrous, transparent crystals melting at 215—216°; it has the specific rotation $[\alpha]_D = +43{\cdot}5$ in a 2 per cent aqueous solution.

98. "*The Resolution of Racemic Tetrahydroparatoluquinaldine into its Optically Active Components.*" By WILLIAM JACKSON POPE and EDMUND MILTON RICH.

The authors have obtained racemic tetrahydroparatoluquinaldine,—

$$\begin{matrix}CMe\cdot CH:C\cdot CH_2\cdot CH_2\\ ||\quad\quad|\quad\quad|\\ CH\cdot CH:C\cdot NH\cdot CHMe\end{matrix},$$

described as an oil by Doebner and Miller (*Ber.*, 1883, xvi., 2464), as a colourless, crystalline substance melting at 32°. It separates in large, transparent crystals from solution in light petroleum, and is almost odourless. The racemic *hydrochloride* crystallises in magnificent prisms melting at 171—173°. Racemic *benzoyltetrahydroparatoluquinaldine*, $C_{11}H_{14}NCOPh$, separates from its solution in acetone in large colourless crystals melting at 103—104°. On adding half a molecular proportion of ammonium dextro-α-bromocamphorsulphonate in aqueous solution to a solution containing one molecular proportion of racemic tetrahydroparatoluquinaldine hydrochloride, *lævotetrahydroparatoluquinaldine dextro α bromocamphorsulphonate*, $C_{11}H_{15}N,C_{10}H_{14}BrOSO_3H$, separates as an oil which soon solidifies; it crystallises from dilute alcohol in colourless needles melting at 195—196°. *Lævotetrahydroparatoluquinaldine*, $C_{11}H_{15}N$, is obtained as a colourless mass on treating its dextromocamphorsulphonate with dilule soda. It separates from its solution in light petroleum in long, colourless, transparent prisms melting at 52—53° having a scarcely perceptible quinoline-like odour; in a 2 per cent solution in benzene at 21°, it has the specific rotation $[\alpha]_D = -80{\cdot}9°$, and the molecular rotation $[M]_D = -130{\cdot}2°$. The *hydrochloride* crystallises in magnificent, colourless crystals melting at 192—194°, and in a 2 per cent aqueous solution at 18° has the specific rotation $[\alpha]_D = -68{\cdot}7°$ and the molecular

rotation $[M]_D = -135{\cdot}3°$. *Benzoyllævotetrahydroparatoluquinaldine*, $C_{11}H_{14}NCOPh$, crystallises from alcohol in colourless prisms melting at 100·5°; in a 2 per cent solution in benzene at 18°, it has the specific rotation $[\alpha]_D = +228{\cdot}8°$ and the molecular rotation $[M]_D = +606{\cdot}4°$. Tetrahydroparatoluquinaldine is homologous with the tetrahydroquinaldine recently resolved by Pope and Peachey (*Proc.*, 1899, xv., 124), and the two bases exhibit interesting relationships. Thus dextro-α-bromocamphorsulphonic acid in both cases separates the lævo-base from the externally compensated mixture. Further, in 2 per cent solutions in benzene, the lævo-bases have the same molecular rotation, viz., $[M]_D = -130{\cdot}20$. Again, on benzoylating the lævorotatory bases, dextrorotatory benzoyl derivatives are obtained, and these have nearly the same molecular rotations in solution in benzene.

99. "*Isomeric Salt of Hydrindamine containing Pentavalent Nitrogen.*" By Frederic Stanley Kipping, D.Sc., F.R.S.

The base, α-hydrindamine, prepared by reducing the oxime of α-hydrindone (König, *Inaug. Diss. Leipzig*, 1899; Kipping and Revis, *Trans.*, 1897, lxxi., 238), combines with bromocamphorsulphonic acid, yielding unequa quantities of two hydrated salts which can be separated by fractional crystallisation. After having been dried at 100°, the more sparingly soluble salt melts at about 150°, the more readily soluble one at about 130°; both compounds have the composition $C_9H_{11}N,C_{10}H_{14}BrO{\cdot}SO_3H$.

Although α-hydrindamine contains an asymmetric carbon atom, and might, therefore, be expected to afford two salts under these conditions, the base regenerated from either of these salts by steam distillation with barium hydrate is optically inactive; the base thus regenerated also gives a hydrocloride and a benzoyl derivative identical in ordinary properties with the corresponding compounds prepared directly from the original externally compensated base. It appears, therefore, that fractional crystallisation of the salt formed with bromocamphorsulphonic acid does not affect a resolution of externally compensated hydrindamine, although this acid been successfully employed by Pope and Peachey (*Proc.*, 1899, xv., 124) for the separation of the optically isomeric tetrahydroquinaldines.

When, moreover, the base regenerated from one of the isomeric salts is treated with bromocamphorsulphonic acid, it again yields a mixture of the two compounds; the salt of lower melting point is also transformed, partly or entirely, into the isomeride by evaporation with a solution of hydrindamine.

The difference between these two isomerides is not purely crystallographic, since both compounds retain their specific properties on repeated crystallisation from water and other solvents; they have also different specific rotations.

Two different salts, apparently analogous to those just described, are also obtained when hydrindamine is combined with chlorocamphorsulphonic acid, but these two compounds have not yet been studied.

Hydrindamine and lævorotatory *cis*-π-camphanic acid (*Trans.*, 1896, lxix., 943), also combine to form two isomeric anhydrous salts having the composition $C_9H_{11}N,C_{10}H_{14}O_4$; the two compounds can be separated by fractional crystallisation, and though very similar in appearance, they differ in melting point by about 20°, the more sparingly soluble one melting at about 190°, the other at about 170°. The base regenerated from one of these salts appears to be inactive, and the isomerism of the two compounds seems to be of the same kind as that of the two salts of bromocamphorsulphonic acid. The more readily soluble *cis*-π-camphanate can be converted into the isomeride by evaporation with excess of a solution of hydrindamine; the specific rotations of the two salts are apparently different.

As it is impossible at present to arrive at any final conclusion as to the cause of the existence of the various isomeric salts briefly described in this note, only the more important facts have been recorded. It may be noted also that the assumption, that the isomerism is due to the pentavalent nitrogen atom being in a position in which its free rotation is prevented, explains some of the facts; another possible explanation is, that autoracemation of the free base occurs with great rapidity, but further experimental evidence is required before either view can be accepted.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.

George Beilby, President.

Annual Meeting, Newcastle, July 12th, 1899.

Outline of the President's Address.

The rapid exhaustion of the British coalfields and the serious increase of smoke pollution make it desirable that the questions of fuel and smoke should be treated simultaneously. Our stores of fuel are being recklessly burned up, while the atmosphere, not only of the large cities, but also of the manufacturing districts outside of these, is being increasingly polluted. To place these questions in their true scale and proportion, it is desirable to allocate the total coal consumption of this country under various heads according to the purposes for which the coal is consumed.

The total coal consumed in the United Kingdom in 1898 was 157 million tons, of which—

76 million tons were consumed for the production of power for industrial purposes;
46 million for the production of heat for industrial purposes;
35 million for the production of heat for domestic purposes.

Taking the first two items more in detail, it is estimated that for the production of *power*—

Railways	consume	10 to 12	million	tons.
Coasting steamers ..	,,	6 to 8	,,	,,
Mines	,,	10 to 11	,,	,,
Factories	,,	38 to 40	,,	,,

For the production of *heat* for industrial purposes—

Blast furnaces ..	consume	16 to 18	million	tons.
Steel and malleable iron works	,,	10 to 12	,,	,,
Other metallurgical works	,,	1 to 2	,,	,,
Chemical works, potteries, and glass works	,,	4 to 6	,,	,,
Gas works	,,	13 to	,,	,,

These figures give a general idea of the magnitude of the problem to be dealt with, and form a sound starting point from which to consider the various remedies which have been suggested. These remedies are broadly divided into two classes.

First.—Improved appliances for the combustion of raw coal, and distribution of the air supply in furnaces.
Second.—The transformation of the raw coal into smokeless fuel by preliminary treatment, either by destructive distillation in gas retorts or in coke ovens, or by its conversion into fuel gas by partial combustion in air and steam.

The distillation of coal in retorts, blast furnaces, and coke ovens was described generally. The amount of each of the crude products obtained from each source was given as below—

Products from the distillation of coal as at present carried on in the United Kingdom.

Gas works distil 13 million tons, and produce—

130,000 million cubic feet of illuminating gas at 650 B.T.U. per cubic foot;
650,000 tons of tar;
129,500 tons of sulphate of ammonia;
7 to 8 million tons of soft coke.

Blast furnaces distil 2 million tons of coal, and produce—

360,000 million cubic feet of fuel gas at 130 B.T.U. per cubic foot;
150,000 tons of tar;
18,000 tons of sulphate of ammonia.

Recovery coke ovens distil 1¼ million tons, and produce—

12,500 million cubic feet of illuminating or fuel gas at 600 B.T.U. per cubic foot;
62,000 tons of tar;
900,000 tons of hard coke;
11,000 tons of sulphate of ammonia.

If beehive ovens were entirely replaced by recovery ovens, there would be a further production of—

125,000 million cubic feet of illuminating or fuel gas;
620,000 tons of tar;
9 million tons of hard coke;
110,000 tons of sulphate of ammonia.

Collecting these figures, together, we have from—

	Tar.	Sulphate of ammonia.
Gas works	650,000 tons	130,000 tons.
Shale oil works	— ,,	37,000 ,,
Blast furnaces	150,000 ,,	18,000 ,,
Recovery ovens	62,000 ,,	11,000 ,,
Present totals	862,000 ,,	196,000 ,,
After extension of recovery ovens	620,000 ,,	110,000 ,,
Probable totals ..	1,482,000 ,,	296,000 ,,

The effects of the natural development of these industries on the markets for by-products were next considered. It was pointed out that, if any considerable part of the 137 million tons of coal which is at present burned in the raw condition were to be converted into gas—two, coke and ammonia—an altogether new condition of things would arise which would need to be foreseen and provided for. A careful study of the whole subject has led to the conclusion that the natural outlet for the coke and pitch would be found in the manufacture of fuel briquettes, and the President advocated the turning of the very best technical skill to the perfecting of this manufacture. He believed that, with skill and enterprise, it would be possible to make briquettes exactly suited for every purpose from boiler firing to domestic cooking.

The leading types of producer for the making of fuel gas were described, from the original "Siemens" to the most recent "Mond" producer.

Coming to the application of the various remedies, it was pointed out that it was now recognised by engineers that steam boilers could be economically and smokelessly fired either by careful hand stoking or by the modern forms of mechanical stoker. In support of this statement, the report of the Committee on Smoke Preventing Appliances, 1895, was quoted from as follows:—"Finally, the Committee are of opinion that, whilst future experiments and inventions may be the means of introducing new and better methods of treatment in the combustion of fuel, enough is known at present to enable steam users to work their boilers with a fair degree of economy and practically without smoke."

It was pointed out that, if the boilers at present in use, which are badly designed and built, were gradually weeded out and replaced by properly designed and built boilers, the burning the 57 million tons of raw coal used for steam raising would be accomplished practically smokelessly. Where small power installations were required, it would be better and more economical to replace steam by gas or electric motors. For railways and coasting steamers, an ample supply of smokeless briquettes could be procured by the extension of the coal distillation industries.

For metallurgical and chemical works of all kinds fuel gas is, in the majority of cases, the most suitable fuel, being smokeless and easily controllable. But he thought it unlikely that the average manufacturer would care to add to his capital expenditure as well as to his anxieties by erecting the comparatively costly plant which is necessary for the satisfactory gasification of raw coal. He thought the time was not far distant when centres for the production and distribution of fuel gas would be established in industrial districts. There was nothing to prevent the economical distribution of fuel gas to works within a mile or two of the producing station. If this were accomplished, the conditions of life in industrial localities would be enormously improved, and in time the smoke blots on the face of the country would be wiped out.

Coming to the 35 million tons of raw coal which is burned for domestic purposes, a good deal of attention was given to the present position of domestic gas firing and its relation to heating and ventilation. The desiderata appeared to be warmth, comfort, and ventilation equal to what is obtainable by the use of an open coal fire, and at a cost not more than twice as great. It was pointed out that the gas fire itself had been brought up to a high standard of excellence, but that it generally suffered in efficiency owing to the unsuitability of its setting and surroundings. In this matter the co-operation of the architect and builder with the gas engineer is required, so that house chimneys and flues may be adapted for gas firing.

For domestic heating the fuel briquette, if properly adapted for that particular purpose, might play an important part in the displacement of raw coal and smoky combustion.

Having thus far shown the magnitude of the fuel and smoke questions in the various departments of industry, and also the various remedies which technical skill has placed at our disposal, the President concluded by inquiring briefly into the reasons why these remedies were being so slowly adopted. He suggested that the self-interest of the manufacturer, as well as his public spirit, need to be aroused. He advocated the application of gentle but uniform pressure for the adoption of smokeless methods on consumers of raw coal by a central authority acting under the Government, and instanced the gradual but steady improvement in the character of the emanations from chemical works which had resulted from the judicious administration of the Alkali Acts during the past thirty years.

As a means of bringing all of the different interests which are concerned in this matter into line, it was suggested that the Society might arrange for the holding of a Conference on the subject of Fuel and Smoke, at which the leading technical societies, as well as the actual industries concerned, should be fully represented.

Mixed Anhydrides of Formic Acid.—A. Béhal.—The author has obtained the whole of the series of mixed anhydrides of formic acid. His present paper contains an account of the preparation of formic acetic anhydride and some of its reactions. A study of the latter leads to the conclusion that aceto-formic anhydride reacts on alcohols, giving only the corresponding formic ethers, with formation of acetic acid.—*Comptes Rendus*, cxxviii., No. 24.

NOTICES OF BOOKS.

Sewage Analysis: a Practical Treatise on the Examination of Sewage, and of Effluents from Sewage. By J. A. Wanklyn and W. J. Cooper. London: Kegan Paul, Trench, Trübner, and Co., Limited. 1899. Pp. 220.

In the introduction the authors draw attention to the great change which has taken place during the now nearly finished century in the disposal of excreta; the convenient method of water carriage has replaced the old-fashioned privy system, but we have now another problem to face, and that is the disposal of the enormous amount of sewage continually being produced. The eight chapters into which about half this volume is divided (the remainder being an appendix dealing with various other matters), deal first with the general analysis of sewage, such as the estimation of specific gravity, chlorine, sulphates, carbonic acid, the ammonia method, &c.; these are all treated in the well known style of one of the authors.

In chapter VI. the authors refer to Sir E. Frankland's combustion process for the estimation of the organic matters in drinking waters. They allege that the process is unsuccessful, and the results impracticable and illusory; but a few lines lower down on the same page they say that as in a typical sewage there would be a 100 m.grms. of organic matter per litre, they can see no insuperable objections to the application of this process to the analysis of sewage.

Now this is not fair to practical chemists; if the authors admit that chemists would be able to measure and estimate 10 parts of organic matter in 100,000 parts of water (as they do), why should they doubt our skill in measuring 0·2 to 0·3 part per 100,000? The difference is not very great, and the smaller amount of gas is much easier to handle.

In the chapter on the utilisation and purification of sewage (No. VIII.) the authors, after reviewing the gradual formation and growth of sewers to our present system as adopted in London, describe their proposed method for the treatment of London sewage. The process is simply that of oxidation, the sewage passing through various tanks so arranged that the ever-changing surface of the sewage shall be exposed to the action of the air for the longest possible time. We see no great objection to it, except that one square mile of tanks would be required.

We are sorry to say that the authors are not friendly to microbes; in fact, a passage in the preface written by one of them would seem to show that he has but a very vague idea as to what they are. He says:—"The wave of fad and fallacy at present passing through the Chemical Society has not disturbed us in our laboratory. Bacteria are interesting creatures, and the study of them is an interesting department of *zoology* and *natural history* (the italics are our own). But bacteria are subject to gravitation and to general physical and chemical action; neither is the burning of the kitchen-fire, nor the action of the steam-engine a manifestation of bacterial action." We never understood that they were.

The book would be greatly improved by the omission of a large amount of *personal* matters which have no interest to the general chemist, and do no good to the authors. There is also evidence of careless proof-reading in many places.

Gutta-percha Trees. ("Les Arbres à Gutta-percha"). By Henri Lecomte, Docteur ès Sciences, Professeur au Lycée Saint-Louis, Lauréat de l'Institut. 1 vol., 8vo. 95 pp. Paris: Georges Carré et C. Naud, 3, Rue Racine.

This volume will be welcomed by the colonists to whom it is addressed. The possibility of cultivating trees yielding gutta-percha on lands hitherto neglected is henceforth no longer a matter of doubt. The consequences of successful acclimatisation are correlative with an immense advance in the manufacturing industry, and it is the duty of all interested in the subject to make themselves acquainted with everything which can aid in their undertaking. M. Lecomte's book, drawn up from information obtained on the spot, and addressed to the planters who are always the first interested in any addition to knowledge on their special subject, will be read with advantage by all engaged in the cultivation of exotic plants.

The increasing importance of gutta-percha in European markets renders this work indispensable to electrical engineers, and to the manufacturer desirous of acquiring accurate information on so valuable a commodity.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, del'Académie des Sciences. Vol. cxxviii., No. 24, June 12, 1899.

Heat of Oxidation of Sodium.—M. de Forcrand.—The author recently published the following numbers:—

$$Na_3 \text{ sol.} + O \text{ gas} = Na_3O \text{ sol.} + 101{\cdot}57 \text{ cal.}$$
$$Na_2 \text{ sol.} + O_2 \text{ gas} = Na_2O_2 \text{ sol.} + 119{\cdot}79 \text{ cal.},$$

and has since re-determined the heat of formation of Na_2O. As a mean of several experiments he obtains the number—

$$Na_2 \text{ sol.} + O \text{ gas} = Na_2O \text{ sol.} + 90{\cdot}985 \text{ cal.}$$

Estimation of Hydrogen Phosphide in Mixture of Gases.—J. Riban.—In a recent paper M. Joannis gave an account of the estimation of phosphoretted hydrogen by means of a solution of copper sulphate, this method being used as preferable to that of absorbing the gas by acid cuprous chloride solution, since the cuprous chloride is liable to attack mercury. The author, referring to this paper, states that for many years he has used this latter method with good results, and finds that cuprous chloride in hydrochloric solution does not attack mercury, for it can be kept in burettes over mercury for days without the mercury meniscus being altered. It is the cuprous chloride, partially decomposed owing to contact with air, which attacks the mercury. This should never be used in analysis.

Action of Iodine on Alkalis.—E. Pechard.—When iodine is dissolved in excess of soda or potash, a yellowish solution is produced, with an odour of saffron and possessing oxidising properties. These facts, together with the thermic phenomena produced when these two substances react on one another, lead to the supposition that there exists a hypoiodite analogous to hypochlorite. The author's experiments confirm this supposition, and he also describes a method of estimating the quantity of hypoiodite formed under these conditions. The quantity of hypoiodite formed is almost proportional to the quantity of soda or potash present. The proportion of hypoiodite decreases very rapidly with the temperature, this salt being transformed into iodate as the temperature rises.

Action of Water on Iodomercurate of Ammonia and Iodomercurate of Potassium.—Maurice François. — The decomposition of the iodomercurate, $HgI_2NH_4IH_2O$, by a large quantity of water, produces a precipitate of mercuric iodide and a solution of ammonium iodide. That of the iodomercurate, HgI_2KI, produces a precipitate of mercuric iodide and a solution of potassium iodide. But NH_4I and KI in solution dissolve HgI_2 to a great extent. The solution becomes saturated

for the temperature of the experiment. This interpretation agrees with observed facts. If the ordinary temperature were 90°, the existence of iodomercurates, $HgI_2.2NH_4I$ and $HgI_2.2KI$ would never have been imagined.

Reduction of Copper at a Low Temperature.—Alb. Colson.—Copper, prepared by the reduction of the oxide by hydrogen at a comparatively low temperature (about 200°), possesses several properties which copper prepared at a high temperature does not. It takes fire when in contact with a drop of dry bromine, and retains this property even when cooled to −21° in methyl chloride, or when placed in a vacuum or dry air, but loses the property when in contact with moist air. Copper prepared in this manner does not give the protoxide of nitrogen when acted on with nitric acid. An examination of the density and magnetic properties of this copper show no variation from ordinary copper.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., November 14, 1898.

Compound of Naphthol and Mercury.—E. Bamberger.—O. Dimroth has lately announced that phenol combines very readily with acetate of mercury; the author noticed the same thing some years ago with β-naphthol, and he described the acetate of β-oxynaphthyle-mercury, which he obtained by adding an acetic solution of β-naphthol to acetate of mercury. It occurs in the form of bright needles, fusing at 185° with decomposition.

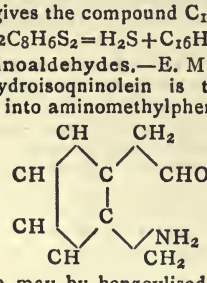
Action of Sulphydrate of Potassium on the Chloride of *o*-Cyanobenzyl. — S. Gabriel and E. Leupold.—A compound, C_8H_7NS, can be prepared by reacting with sulphydrate of potassium on the chloride of *o*-cyanobenzyl; but this compound is easily transformed in the presence of an excess of sulphydrate of potassium into $C_{16}H_{10}S_3$, which can also be prepared directly; it is undoubtedly formed according to the equation $2CN-C_6H_4-CH_2-SH + H_2S = 2NH_3 + C_{16}H_{10}S_3$; but the mechanism of this decomposition, as well as the constitution of the substance being unknown, the authors undertook to determine them; they arrived at the conclusion that an intermediate product must be formed, and they succeeded, in fact, in preparing dithiophthalide,—

$$C_6H_4<\begin{matrix}CH_2\\CS\end{matrix}>S,$$

which, when left in alcoholic solution with sulphydrate of potassium, gives the compound $C_{16}H_{10}S_3$.

$$2C_8H_6S_2 = H_2S + C_{16}H_{10}S_3.$$

On the Aminoaldehydes.—E. Maas and R. Wolffenstein.—Tetrahydroisoqninolein is transformed by the action of H_2O_2 into aminomethylphenylacetaldehyde,—



This aldehyde may by benzoylised, but, instead of obtaining by the oxidation of this new derivative a benzoylised acid, it is observed that the benzoyl group is eliminated. The authors have studied the most simple type of the amino-aldehydes with amino-valeraldehyde obtained by the oxidation of piperidine by H_2O_2. They observed that the benzoylised derivative of this aldehyde eliminated the benzoyl group under the influence of permanganate of potash.

On 3 : 8-Diamidodiphenyl-2 : 9-Dicarbonic Acid.—C. Bulow and U. von Reden. — Benzidine-*o*-dicarbonic acid has acquired a certain importance in the arts from the fact that it serves as the primary material for the manufacture of 2 B naphthyle blue. It is prepared by reducing in alkaline solution the *o*-nitro-benzoic acid, and by transposing the hydazoic compound which results by boiling with concentrated HCl; 3 : 8 diamido diphenyl-2 : 9 dicarbonic acid acts by Schotten-Baumann's method with chloride of benzoyl or acetic anhydride, giving the corresponding dibenzoylised or diacetylised derivatives.

Synthesis of some Naphtindulines. — O. Fischer and E. Hepp.—Dinaphtophenylaposafranine is formed by the reaction of HCl nitrosophenyl-α-naphthylamine on phenyl-β-naphthylamine, in the presence of acetic acid on the water-bath. It crystallises in deep violet flakes fusible at 256° or in voluminous needles fusible at 268°. At 130° with alcoholic ammonia this base divides into aniline and rosonaphtindone. (*m*.N)-Ethyldinapthophenylaposafranine is prepared like the preceding base, by using ethyl-β-naphthylamine. It crystallises in needles with iridescent green reflections, fusible at 255°. Under the influence of concentrated HCl at 210°, it loses $NH_2C_6H_5$, and gives a dinaphthoaposafranone ethyl fusible at 247°. (*m*.N)-ethyldinaphthoaposafranine is obtained by treating phenylised safranine with alcoholic ammonia at 120—130° These salts crystallise well with HCl and HNO_3.

City and Guilds of London Institute.—Central Technical College.—The Old Students' Association of the College held its Annual Dinner on Thursday, July 6th, at the Restaurant Frascati; the Dean of the College, Professor Armstrong, taking the chair. A large number were present, including the Professors, a number of the Junior Staff, Sir Philip Magnus, Director of the Technological Examination Department, and Mr. A. L. Soper, Assistant Secretary to the Institute. Professor W. E. Ayrton, in proposing the toast of the Association, referred to the progress of the College, and the insufficiency of accommodation due to the continued increase in the number of students; he announced that the Electrical Department would soon be greatly extended by the erection of a large new Dynamo Room nearly six times the size of that at present in use, and occupying a considerable part of the ground floor of the new building of the Royal School of Art Needlework, adjoining the College. The accommodation for this department would be further increased by the completion of a new drawing office and a new lecture theatre. The toast was replied to by Mr. Maurice Solomon, Secretary of the Association. Sir Philip Magnus, in proposing the toast of the College and its Professors, said that when first he had the honour of drawing up the scheme of the College it was prophesied that nobody would go to South Kensington to learn Engineering. But in spite of the fact that they had a harder entrance examination than any other institution of the kind, there were now 250 students in a building only designed for 200. The College was that day entering on a new period in its career, for it was likely to become an integral part of the new University of London, which had decided the day before to move into new quarters at the Imperial Institute, next door to the College. The needs of the College were recognised in the new University by the decision to appoint a faculty of Engineering for the first time in the history of University education, and by the variation of the University Matriculation Examination to suit the requirements of different classes of students. The toast was replied to by Prof. Henrici. The toast of the Athletic Clubs was proposed by Mr. F. S. Miller, who remarked that the prospects of the College Athletics were in a more favourable state owing to the Students' Union having obtained an Athletic ground. Mr. F. C. Hounsfield responded. The toast of the Chairman was proposed by Mr. N. C. Sawers, and Prof. Armstrong in reply alluded to the value of the research work done at the College, especially in relation to the difference between the spirit it introduced and that due to the importance given to text-book information by University Education. A musical programme was supplied by Messrs. Stanger, Mayes, Hounsfield, Trier, Tisdall, Sawers, and Plunket.

THE CHEMICAL NEWS.

VOL. LXXX., No. 2069.

THE ACTION OF HYDROGEN ON SULPHIDE OF SILVER; AND THE INVERSE REACTION.

By H. PÉLABON.

SULPHIDE of silver can be reduced by hydrogen. This fact was established in 1879 by M. Margottet; he showed that it was sufficient to heat crystallised sulphide of silver for some hours towards 500° in a sealed tube, in an atmosphere of hydrogen, to see that the reduction takes place at various points throughout the mass. The silver set at liberty is in the form of very fine wire similar to filiform native silver.

Inversely sulphydric acid attacks metallic silver.

M. Berthelot (*Am. Chim. Phys.*, Series 5, xvi., p. 440) has verified the fact that sulphuretted hydrogen is decomposed by silver towards 550° with the formation of the metallic sulphide and hydrogen.

We propose studying these two inverse reactions for very wide variations of temperature.

Sealed tubes containing sulphuretted hydrogen and silver, or hydrogen and sulphide of silver, are kept for a sufficiently long time at a definite temperature. At the end of this time they are quickly withdrawn from the furnace, and cooled rapidly by whirling in the air at the end of an iron wire to which they are attached.

The analysis of the gaseous mixture contained in the tubes thus cooled gives the proportion of sulphuretted hydrogen they contain at the temperature of the experiment.

In an experiment in which hydrogen and sulphide of silver were originally present, there is formed, at a temperature of above 250°, sulphuretted hydrogen, the proportion of which in the mixture increases from the first with the time, and then remains steady.

In a tube containing, on the contrary, sulphuretted hydrogen and metallic silver, the proportion of sulphuretted hydrogen diminishes by reason of the formation of sulphide of silver and hydrogen up to a certain limit.

Temperatures above 280°.—For equal temperatures above 280° the two limits are identical. The two reactions in question are limited, and under such conditions of temperature we notice a series of states of equilibrium of the system; silver, sulphide of silver, hydrogen, and sulphuretted hydrogen.

These states can, for example, be characterised by the value of the relation between the partial pressure of the sulphuretted hydrogen in the gaseous mixture and the total pressure of the mixture. Let us call this relationship ρ.

We have said that the value of this relationship diminishes slowly as the temperature increases. In other words, if we represent the successive states of equilibrium of the system by a curve so constructed that the abscissæ are the degrees of temperature, and the ordinates the corresponding values of ρ, the points of this curve should approach the axis of the abscissæ as the temperature increases.

A very simple experiment confirms this view. We prepare two sealed tubes, each divided into two parts by a contraction, in one part we place sulphide of silver, in the other silver; both tubes also contain dry hydrogen gas. The two tubes are heated at the same time in the same furnace, but they are so arranged that the two parts of each tube are at different temperatures, 440° and 350° for example. In one of the tubes it is the sulphide of silver which is at 440°, in the other it is the silver.

The experiment shows that in the first tube the silver remain bright, it is not attacked by the sulphur; in fact, as we have said before, the quantity of sulphuretted hydrogen produced at 440° is but little less than that which should be present in the mixture to attack the silver at 350°. We observe that filiform silver is formed, but it soon ceases to develope.

In the other tube the silver becomes tarnished, and the filiform silver which occurs on the sulphide continues to develope as time proceeds. The quantity of sulphuretted hydrogen produced at 350° is in fact greater than that which should be present in the mixture to attack the silver; this latter destroys a part of this sulphuretted hydrogen forming sulphide, and the hydrogen thus set at liberty reacts again on the sulphide.

The portion of the curve which our experiments have enabled us to trace might be taken for a straight line between 360° and 700°. Between 280° and 360° the points of the curve are situated a little above the straight continuation of the preceding one.

The ordinates of the points of this straight line, of which the abscissæ correspond to the temperatures 360° and 700°, are respectively $\rho = 0{\cdot}21$, and $\rho = 0{\cdot}16$

At 280° we find $\rho =$ about $0{\cdot}25$. These results are in complete accord with the law of the displacement of equilibrium by variations of temperature, if we admit the following reaction—

$$Ag_2S(\text{crystallised}) + H_2(\text{gaseous}) = H_2S(\text{gaseous}) + Ag(\text{solid}),$$

a reaction which, at 15°, is accompanied by a disengagement of heat equal to 1·6 calories, and is still exothermic at the temperature of our experiments.

Remarks.—It is not necessary for all parts of the tube to be maintained at the same temperature; the results are absolutely the same if we content ourselves with treating that portion of the tube only which contains the morsel of silver, or sulphide of silver. Equilibrium is reached in such a case in a little longer time, but the limit is characterised by the same value of ρ.

Whatever be the initial conditions equilibrium is reached after heating for a so much longer time as the temperature is lower. While at 580° equilibrium is established in a few minutes, at 440° it requires about forty hours, and at 360° about sixty hours.

At temperatures below 350° both reactions take place with extreme slowness; thus, for example, at 280° it requires about three thousand hours for the sulphuretted hydrogen to cease forming in a tube containing originally sulphide of silver and hydrogen. To increase the speed we introduced into the sealed tubes mixtures of known composition of hydrogen and sulphuretted hydrogen, and we were thus enabled to determine for a given temperature, what mixture remains unchanged in the presence either of silver or of sulphide of silver. It suffices to heat the tubes for ten or fifteen days to notice a change of composition in the systems either too rich or too poor in sulphuretted hydrogen.

On the contrary, at temperatures above 580°, equilibrium is established in a time comparable with the time taken to cool the tubes; from this observation it results that the rapid method of cooling need not necessarily be adopted, It would give much too high figures for the value of ρ. To get over the difficulty we used partly heated tubes of which one end, being outside the furnace, was at a sufficiently low temperature that it could be held in the hand. Equilibrium was established in a similar tube; it was withdrawn quickly from the furnace, and allowed to cool by holding the hot end upwards; the piece of sulphurised silver then fell from the heated part. On contact with the cold glass and cold gas it cools very rapidly; it is then in the presence of a gaseous mixture at a relatively very low temperature, and which can only act on it to a very small degree. But even allowing that a very slight reaction takes place, the amount of sulphuretted hydrogen produced or decomposed would

hardly effect the composition of the gaseous mass in the tube.

By using this method the experiments were only limited, at about 700°, by the softening of the glass.

It may be mentioned that for a known degree of temperature, the limit of the value ρ is independent of the physical state of the silver or of the sulphide of silver. We took pure silver in sheets, in foil, and finely divided, prepared by reducing the chloride in ammoniacal solution by pure zinc. We have used sulphide of silver crystallised and precipitated, either simply dried or dried and melted. All these bodies have, with the same temperature, given us the same value for ρ. This value is still the same if we first put into the sealed tube, quantities of hydrogen, silver, and sulphurtinsufficient to completely sulphurise the silver.

Remarks on the formation of Filiform Silver.—We have observed that in the reaction of hydrogen on sulphide of silver in sealed tubes, the silver set at liberty only takes the form of filaments when the temperature is below 580°, and consequently at temperatures for which the reduction is not produced too rapidly. At temperatures above 580°, the pieces of sulphide of silver become covered with an almost uniform layer of metallic silver. The most beautiful samples of filiform silver are those obtained by heating crystallised sulphide of silver and hydrogen in a sealed tube to about 400°. At 280° the extremely slow reduction of the sulphide of silver is again accompanied by the production of very fine filaments of silver. In every case filiform silver ceases to be produced when equilibrium is reached. If we take the precaution to place in one part of the tube a certain quantity of lead, so as to continuously decompose the sulphuretted hydrogen formed, the regenerated hydrogen gas will act on a fresh portion of sulphide of silver; under these conditions we note that the silver filaments increase in length as long as there is any undecomposed sulphide of silver remaining. These filaments reach a length of 5 or 6 c.m.; they start at a very limited number of points on the surface of the sulphide, more especially if the latter has been first melted. As a rule their number does not increase; that is to say, the sulphide is only reduced at the point where it is in contact with the extremity of a filament of silver; the metal set at liberty drives before it the filament already formed, and thus the length increases. We have had in the course of our experiments the opportunity of seeing the reduction taking place with five, three, and even one filament of silver.

Temperatures below 280°.—We are able to assert that at the ordinary temperature, when the gas is thoroughly dry, no sulphuration of the silver by sulphuretted hydrogen takes place. Silver is not attacked by sulphuretted hydrogen below a temperature of 180°.

Tubes have been kept for six months at 180°, containing strips of pure silver and known mixtures of hydrogen and sulphuretted hydrogen. The results were the following:—

Composition of the mixture placed in the tube.	Composition of the mixture after two months at 180°.
$\rho = 0{\cdot}7011$	$\rho = 0{\cdot}7085$
$\rho = 0{\cdot}6238$	$\rho = 0{\cdot}6258$
$\rho = 0{\cdot}4651$	$\rho = 0{\cdot}4651$
$\rho = 0{\cdot}2100$	$\rho = 0{\cdot}2117$

We see from these figures that the quantity of sulphuretted hydrogen has not diminished.

We have also noticed that sulphide of silver is no longer attacked by hydrogen within these limits of temperature; to observe this we placed in a sealed tube a piece of sulphide of silver, a piece of polished pure copper, and some hydrogen gas. The tube was kept at 180° for one month; the surface of the copper was in no way tarnished. If reduction had taken place, even to a very slight extent, the sulphuretted hydrogen would have formed black sulphide of copper, which would have distinctly changed the appearance of the metal.

To sum up:—1. Below 180° silver is not attacked by dry sulphuretted hydrogen. Neither is sulphide of silver reduced by hydrogen.

2. Above 280° the two reactions take place with a speed so much the greater as the temperature is higher, but they are limited. The two limits led to the same value of temperature and the same composition of the gaseous system. This composition limit varies very little with the temperature; the gaseous mixture obtained is the richer in sulphuretted hydrogen as the temperature is lower.

3. The silver set at liberty by the reduction of the sulphide is filiform when the operation takes place at a temperature below 580°. At higher temperatures, the silver formed covers the surface of the sulphide uniformly.

There remains to examine what takes place between 180° and 200°: we are at the present time following this up.—*Bull. Soc. Chim.*, Series 3, xxi., No. 9.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during this month shows a still further deficit; rain fell on five days only, the total amount being 1·05 inches. As the average amount for the past thirty years is 2·11 inches, we have a deficit of 1·06 inches, bringing the total deficit for the first six months of the year to 1·75 inches, or 15·8 per cent on the average rainfall.

Our bacteriological examinations of 382 samples have given the results recorded in the following table; we have also examined 48 other samples, from special wells, standpipes, &c., making a total of 430 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	408
New River, filtered (mean of 77 samples) ..	20
Thames, unfiltered (mean of 26 samples) ..	1677
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 201 samples)	30
Ditto ditto .. .. highest	372
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	1225
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	19

The bacterial and chemical quality of the Metropolitan waters during June has remained at the same high standard of purity that has characterised it during the last three months. Deficient rainfall may partly account for this improvement, but some of the excellent quality of the water is undoubtedly due to the more efficient regulation of the filtration which is now possible, on account of the large number of bacterial examinations of the Companies' filter wells.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THE INFLUENCE OF HYDROCHLORIC ACID IN TITRATIONS BY SODIUM THIOSULPHATE,

WITH SPECIAL REFERENCE TO THE ESTIMATION OF SELENIOUS ACID.*

By JOHN T. NORTON, Jun.

In the method of Norris and Fay (*Am. Chem. Journ.*, xviii., p. 703) for the iodometric determination of selenious acid, advantage is taken of a direct and unique action of sodium thiosulphate upon selenium dioxide in the presence of hydrochloric acid. Most excellent results are claimed for this method; but the explicit statement of the originators of the method, that the amount of hydrochloric acid present does not influence the result, provided the titration is made at the temperature of melting ice, is so extraordinary in view of generally accepted ideas in regard to the interaction of hydrochloric acid and sodium thiosulphate, as to suggest the necessity of careful investigation of this point.

Pickering (*Journ. Chem. Soc.*, xxxvii., p. 135), in his investigation of the reaction between iodine and sodium thiosulphate, has shown that more iodine is required to oxidise the thiosulphate as the proportion of hydrochloric acid increases. He ascribed this effect to the formation of a sulphate, apparently, by the increased activity of the iodine, but the more rational explanation is that, although some sulphate is ultimately formed, the thiosulphate is first partially decomposed into free sulphur and sulphur dioxide. Finkener ("Anal. Chem.," 6 Aufl., p. 620) and Mohr ("Titrirmethode," 6 Aufl., p. 279) also mention the decomposing effect of free acid upon sodium thiosulphate.

The sodium thiosulphate used in the following experiments was taken in nearly decinormal solution and was standardised by running it into an approximately decinormal solution of iodine, the value of which had been determined by comparison with decinormal arsenious acid made from carefully re-sublimed arsenious oxide. In the experiments of Table I. the solutions were stirred continuously and kept at a temperature of from 0° to 5° C., while the thiosulphate ran into the acidified liquid. The volume of the solution, though fixed at the beginning as given in the table, was considerably increased during the operation by the melting of the ice. Titrations were conducted as rapidly as possible to avoid the separation of sulphur, which is likely to occur, especially when the acid and thiosulphate are present in large quantities. A perusal of the table shows that the influence of the hydrochloric acid upon the thiosulphate depends chiefly upon the amount of the thiosulphate present and afterwards upon the degree of dilution and its own absolute quantity. Thus when 30 c.m.³ of sodium thiosulphate were employed the effect of 10 c.m.³ of acid is marked at all dilutions within the range of the experiments; the effect of 5 c.m.³ of acid is inappreciable only at a dilution of from 400 to 500 c.m.³, and when 1 c.m.³ of acid is employed the effect is only perceptible at a volume of 100 c.m.³. When 25 c.m.³ of the thiosulphate were used the influence of the acid is less marked; for at a dilution of 500 c.m.³ the effect of 10 c.m.³ of acid is not seen, and 20 c.m.³ of the thiosulphate may be present at any dilution down to 100 c.m.³ in the presence of as much as 10 c.m.³ of the acid, and even considerably more, as experiments not included in the table indicated.

Table I.

Volume of liquid at beginning of titration.	$Na_2S_2O_3$ approximately $n/10$ taken.	Volume of N/10 iodine used in titration.			
		HCl = none.	= 1 c.m.³.	= 5 c.m.³.	= 10 c.m.³.
C.m.³.	C.m.³.	C.m.³.	C.m.³.	C.m.³.	C.m.³.
100	30	30·25	30·75	30·76	31·2
200	30	30·22	30·21	30·56	31·4
300	30	30·20	30·22	31·03	30·9
400	30	30·21	30·20	30·20	30·55
500	30	30·20	30·20	30·21	30·55
	Mean =	30·22			
100	25	25·29	25·32	25·98	25·70
200	25	25·28	25·34	25·40	25·45
300	25	25·29	25·41	25·38	25·83
400	25	25·27	25·24	25·30	25·63
500	24	25·22	25·23	25·40	25·30
	Mean =	25·27			
100	20	20·15	20·17	20·33	20·23
200	20	20·20	20·13	20·27	20·23
300	20	20·21	20·15	20·20	20·17
400	20	20·20	20·10	20·27	20·07
500	20	20·10	20·10	20·17	20·13
	Mean =	20·15			

The slight discrepancies which appear occasionally in the table were due, no doubt, to unavoidable differences in the time of action.

This influence of time upon the reaction between sodium thiosulphate, iodine, and hydrochloric acid comes out clearly in the following series of experiments, in which the thiosulphate was run into the acidified water, cooled to a temperature of from 0° to 5° C. by means of ice, the solution being allowed to stand five, ten, and fifteen minutes. Sulphur was thrown down in nearly every case.

Table II.

Volume of the liquid at beginning of titration.	HCl (sp. gr. 112) present.	$Na_2S_2O_3$ approximately N/10 taken.	Volume of N/10 iodine used in titration after standing—		
			Five minutes.	Ten minutes.	Fifteen minutes.
C.m.³.	C.m.³.	C.m.³.	C.m.³.	C.m.³.	C.m.³.
200	10	30	30·80	31·30	32·32
200	10	25	25·50	26·00	26·30
200	10	20	20·30	20·70	20·68

The results of the table emphasize sufficiently the necessity of proceeding as rapidly as possible with the titration of sodium thiosulphate by iodine in presence of hydrochloric acid, when the thiosulphate is present in considerable amount. As would be expected, the effect of temperature upon the reaction is also marked. In the following experiments the sodium thiosulphate was run into the acidified water, previously heated to the temperature indicated, and then titrated with iodine.

From these results it is plain that the conditions under which considerable amounts of sodium thiosulphate are titrated in presence of hydrochloric acid must be carefully guarded when accuracy is a consideration. It is also apparent that in all cases the temperature should be reduced as nearly to 0° C. as possible, and rapidity of titration by the iodine is an essential. So long as the

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Series 4, vol. vii., April, 1899.

Table III.

Volume of liquid at beginning of titration.	HCl (sp. gr. 112) taken.	Temp. Centigrade.	$Na_2S_2O_3$ approximately N/10 taken.	Volume of N/10 iodine used in titrations at different temperatures.
C.m.³.	C.m.³.		C.m.³.	C.m.³.
400	10	6°	25	23·52
400	10	22°	25	23·73
400	10	34°	25	24·35
400	10	42°	25	24·5
400	10	54°	25	25
400	10	64°	25	26·1

thiosulphate present does not exceed 20 c.m.³ of the *n*/10 solution, rapid titration in cold solution proceeds with fair regularity in presence of hydrochloric acid up to 10 c.m.³ of the acid of sp. gr. 112. When, however, the amount of thiosulphate is greater than 20 c.m.³ of the *n*/10 solution, care as to the restriction of the acid and dilution of the solution becomes a necessity. Fortunately, in most analytical processes involving the use of the thiosulphate it is possible to add that reagent from the burette to the solution to be acted upon, so that it is destroyed normally as fast as it is introduced, and the danger of interaction with the acid does not occur. In the process of Norris and Fay, however, the method involves the addition of an excess of the thiosulphate to the solution of selenious and hydrochloric acids, and thus the conditions prevail which demand care as to the relation of the acid, the thiosulphate, and the degree of dilution. I have experimented, therefore, with this process under varying conditions.

The process of Norris and Fay for the iodometric determination of selenious acid consists briefly in treating the solution of that acid in ice-water, in the presence of hydrochloric acid, with an excess of a *n*/10 solution of sodium thiosulphate and titrating back the excess of the thiosulphate with iodine. Four molecules of sodium thiosulphate act, apparently, upon one molecule of selenious acid according to a reaction which the authors propose to study.

The selenium dioxide used was made by dissolving presumably pure selenium in nitric acid and evaporating to dryness. The residue was then treated with water, and a little barium hydroxide was added to remove any sulphate which might be present. The solution was then filtered and the filtrate evaporated to dryness. The residue was mixed with four or five times its volume of dried pulverised pyrolusite, and the whole was put into a porcelain crucible and heated. The sublimate of selenium dioxide was carefully collected on a dry watch-glass and put into a drying-bottle as quickly as possible. The pyrolusite prevents any reduction of the selenium dioxide to selenium and the product consisted of beautiful long white needles. This method of preparing the selenium dioxide, which has been used for some time in this laboratory, avoids contamination of the selenium dioxide by nitric acid or water, resulting from the decomposition of the latter, which would be possible in case this reagent were employed in the final sublimation, as is recommended by Norris and Fay. The hydrochloric acid used was of sp. gr. 112, as recommended by the originators of the process. For the experiments of Table IV. the dilution at the beginning was fixed at 400 c.m.³, and this was increased in every case by the melting of the ice used to cool the liquid. A glance at the preceding part of this paper will show that at this degree of dilution the hydrochloric acid present has the least effect.

These results, while not so good as those obtained by Norris and Fay, are satisfactory, and show that at this degree of dilution the process is accurate. These results accord closely with those contained in Table I. At a dilution of 400 c.m.³ or in the presence of only 20 c.m.³ of sodium thiosulphate in excess the hydrochloric acid present had no perceptible effect. Of course, it must be kept in mind that the hydrochloric acid acts only upon the excess of thiosulphate which is not taken up by the

Table IV.

	Amount SeO_2 taken.	HCl sp. gr. 112 taken.	Volume at beginning of titration.	Excess $Na_2S_2O_3$ employed.	SeO_2 found.	Error.
	Grm.	C.m.³.	C.m.³.	C.m.³.	Grm.	Grm.
1.	0·0616	10	400	2·28	0·0625	0·0009+
2.	0·0628	10	400	7·11	0·0631	0·0003+
3.	0·0508	10	400	11·4	0·0511	0·0003+
4.	0·0587	10	400	12·8	0·0594	0·0007+
5.	0·0807	10	400	15·3	0·0813	0·0006+
6.	0·0633	10	400	20·85	0·0638	0·0005+
7.	0·0682	25	400	1·11	0·0685	0·0003+
8.	0·0779	25	400	1·35	0·0788	0·0009+
9.	0·0465	25	400	18·93	0·0469	0·0004+
				Mean		0·00005+

selenium dioxide. The slight constant plus error in these results cannot be accounted for by errors in the standards; they were all carefully determined. Another preparation of selenium dioxide was made, starting with pure selenium carefully precipitated by sulphurous acid, before putting it through the course of treatment previously described, and the results obtained by the action of the sodium thiosulphate recorded in Table V. agree closely with those of the preceding table.

Table V.

	Amount SeO_2 taken.	HCl sp. gr. 112.	H_2O at beginning.	$Na_2S_2O_3$ in excess.	SeO_2 found.	Error.
	Grm.	C.m.³.	C.m.³.	C.m.³.	Grm.	Grm.
1.	0·0562	10	400	9·52	0·0566	0·0004+
2.	0·0651	25	400	11·20	0·0655	0·0004+

The next step was to determine the effect of diminishing the dilution and of varying the strength of acid. The following table gives the results of my experiments.

Table VI.

	Amount of SeO_2 taken.	Volume of H_2O at beginning.	HCl (sp. gr. 112).	Excess of $Na_2S_2O_3$.	SeO_2 taken.	Error.
	Grm.	C.m.³.	C.m.³.	C.m.³.	Grm.	Grm.
1.	0·1042	200	5	24·16	0·1041	0·0001−
2.	0·0611	200	10	13·3	0·0611	0·0000±
3.	0·0850	200	10	21·9	0·0828	0·0022−
4.	0·0757	200	25	13·07	0·0749	0·0008−
5.	0·0540	200	25	21·02	0·0522	0·0018−
6.	0·0674	300	5	10·04	0·0679	0·0005+
7.	0·2416	400	5	15·9	0·2424	0·0008+

It is apparent that at the dilution of 200 c.m.³ we run into difficulties, and the greater the excess of thiosulphate present the greater is the error. When the amount of sodium thiosulphate exceeds 20 c.m.³ a reduction in the amount of acid to 5 c.m.³ is plainly of advantage, as is shown in a comparison of Experiments 1, 3, and 5, and is not disadvantageous at larger dilutions and with smaller amounts of the thiosulphate, as shown in Experiments 6 and 7. The necessity of placing some limits on the method of Norris and Fay has now, I think, been established. The excess of the thiosulphate must be carefully regulated, as well as the temperature. If one has knowledge of the approximate amount of selenious acid in solution, this is not a matter of great difficulty, and things should be so arranged that no more than 20 c.m.³ of the *n*/10 thiosulphate should ever be present in excess of the amount necessary to reduce the selenious acid. If this limit—amounting to 0·0400 c.m. of SeO_2—is placed upon the thiosulphate, so much as 10 c.m.³ of hydrochloric acid (sp. gr. 112) may be present without endangering the accuracy of the process, provided the solution is diluted to 400 c.m.³ at the outset; if only 5 c.m.³ of hydrochloric acid are present, the volume at the beginning may be reduced with safety to 200 c.m.³. At all events, 5 c.m.³ of the hydrochloric acid are amply sufficient to bring about the reaction between the thiosulphate and the selenium

at any dilution within the range of my experiments. With these precautions taken, the process of Norris and Fay is simple, rapid, and accurate; without them, as the experimental results indicate, errors of considerable amount may enter.

According to the method of Muthmann and Shafer (*Berichte d. D. Chem. Gesell.*, xxvi., 1008), the determination of selenious acid is effected by the simple addition of potassium iodide to the acidulated solution of selenious acid, and the iodine set free is titrated with sodium thiosulphate. In this procedure the thiosulphate is taken up by the iodine as it is added to the solution, so that the danger of any action between the thiosulphate and the acid is out of the question. It was shown in a former paper from this laboratory (Gooch and Reynolds, *Amer. Journ. Sci.*, I., 254) that this simple method is inaccurate on account of the incompleteness of reduction in the cold and in presence of the iodine evolved. In a later article, also from this laboratory (Peirce, *Amer. Journ. Sci.*, i., 1896, p. 416), it was shown that selenium may be completely precipitated and determined with accuracy gravimetrically provided the amount of potassium iodide employed is enormously in excess of that theoretically required. This suggests naturally the trial of very large excesses of potassium iodide in the process of Muthmann and Shafer. The details of experiments made in this manner are given in the following table:—

TABLE VII.

	SeO_2 used.	KI.	Volume of solution.	HCl (sp. gr. 1·12).	SeO_2 found.	Error.
	Grm.	Grm.	C.m.³.	C.m.³.	Grm.	Grm.
1.	0·0553	10	150	10	0·0558	0·0005+
2.	0·0574	5	150	10	0·0567	0·0007−
3.	0·0683	5	150	10	0·0683	0·0000±
4.	0·0487	5	150	10	0·0484	0·0003−
5.	0·2617	10	150	10	0·2589	0·0028−

It is obvious that for small quantities of selenium dioxide the accuracy of the process is very much increased by the use of large amounts of iodide, though, of course, the difficulty in reading the end-reaction due to the presence of precipitated red selenium still remains; but the process is still inaccurate when large amounts of selenium dioxide are employed.

In conclusion, I wish to thank Prof. F. A. Gooch for his kind advice and assistance.

THE BLUE PIGMENT IN CORAL (*HELIOPORA CŒRULEA*) AND OTHER ANIMAL ORGANISMS.*

By A. LIVERSIDGE, M.A., LL.D., F.R.S.,
Professor of Chemistry in the University of Sydney.

THE following notes contain the results of some preliminary experiments upon the blue pigment present in the blue coral known as *Heliopora cœrulea*. Some fragments of the coral were supplied to me by Professor David, which had been collected by him at Funafuti, when conducting the Coral Reef Exploration Expedition in 1897. He states that the *Heliopora cœrulea* is there very abundant in places.

The occurrence of the blue colouring matter in this coral is drawn attention to by the late H. N. Moseley, F.R S., in the "Challenger Reports,"† who points out that it can be partly separated by dissolving away the calcareous matter by means of hydrochloric acid, and dissolving the pigment in alcohol—he, however, did not obtain it in a pure form nor did he ascertain its chemical composition: but he gives a full account, illustrated by drawings, of the way in which it occurs in the coral. He states:—"The blue tint is seen in sections of the corallum of *Heliopora cœrulea* to be diffused within the hard tissue. The colour is faint or almost absent in the freshly-growing tips of the corallum, and pale in the most recently formed superficial structures generally; it is darkest in the layer lying immediately beneath these, that is to say, in the most recently matured tissue.

"In transverse sections it is seen to be darkest at the surfaces of the walls of the tubes and calicles. In vertical section of the corallum the continuation of the dark blue line marking the margin of the wall of each tube enables the line of the tube to be traced past the superadded tabula, and marks the boundary between the two structures. Very exceptionally, intensely blue streaks are developed more internally on either side of the central canal. The tabulæ are almost colourless."

Separation of the Pigment.

On shaking the finely powdered coral with water, the blue pigment does not float, as might have been anticipated, but rather tends to collect at the bottom of the vessel; not sufficiently, however, to be used as a means of separating and collecting it.

As stated by Moseley the readiest way to separate the pigment from the mineral matter of the coral is to dissolve the coral in hydrochloric acid, when the blue colouring matter mixed with animal matter is left in suspension; it can be then filtered off from the calcium chloride solution, which passes through the filter in a colourless condition.

Some of the pieces of coral were old and water-worn, "dead" coral: a specimen of this dissolved in pure hydrochloric acid left a small quantity of insoluble residue amounting to about 0·2 per cent; under the microscope this was seen to consist of rock debris, probably pumice, and a few crystals and groups of crystals of magnetite.

One specimen of such "dead" coral yielded 0·267 per cent of the crude pigment after drying in a water oven. A specimen of the unrolled or "live" coral yielded 1·123 per cent of the dried pigment; the greater yield from the "live" coral appears to be due to the larger amount of animal matter mixed with the pigment.

The crude pigment as set free from the coral by hydrochloric acid is black in colour, and on drying splits up into small pieces with very lustrous conchoidal surfaces, and it is exceedingly tender and so brittle that on crushing much of it flies out of the mortar.

On ignition the pigment gives off nitrogenous odours, intumesces greatly, and the charred residue acquires deep blue, green, and other iridescent colours, similar to those sometimes seen on coke and specimens of hæmatite: this sheen did not readily burn off. No crystalline structure could be detected in the intumesced char—(indigo, if present, would probably have been sublimed and deposited in the cavities, it was accordingly specially searched for)—finally a bulky ferruginous-looking ash was left. The ash was found to contain much phosphoric acid, together with iron, lime, and magnesia.

Moseley states that the blue colouring matter left by hydrochloric acid can be *at once* dissolved off the filter by alcohol; this may be the case with the perfectly fresh coral, but I found that the colour from the old dead coral is only slightly soluble, and even absolute alcohol only dissolves it in part. On evaporation, this extract leaves a dark olive-green residue (indigo leaves a blue residue), which intumesces on ignition and leaves a little ash.

To ascertain its solubility 0·648 grm. of the blue residue left by hydrochloric acid was extracted for some hours with 75 c.c. of absolute alcohol in a percolator over a water-bath; the dark green alcoholic extract when evaporated to dryness in a platinum dish over a water-bath, left a dull dark green liquid coloured and blistered residue weighing 0·115 grm., equal to 17·8 per cent on the crude pigment, and to 0·18 per cent on the original coral,

* Read before the Royal Society of N. S. Wales, December 7, 1898.

† "Zoology," vol. ii., p. 109; see also H. N. Moseley, "On the Colouring Matters of Various Animals, and especially of Deep Sea Forms Dredged by H.M.S. *Challenger*."—*Quart. Journ. of Micro. Soc.*, New Series, January, 1877, vol. xii., p. 2.

On warming, it melts and becomes very fluid, but solidifies on cooling; at higher temperatures it gives off much fume and a disagreeable nitrogenous odour like burnt fish and finally inflames; the carbon burns off very quickly, and some ash is left, viz., the above 0·115 grm. of pigment left 0·0061 grm., or 5·33 per cent. This ash dissolved in hydrochloric acid to a pale yellow colour, and was found to contain iron, phosphoric oxide, lime, and magnesia; the quantity (0·0061 grm.) was insufficient for a complete examination.

Next, 0·648 grm. of the blue colouring matter left by hydrochloric acid was placed in a percolator with 60 c.c. glacial acetic acid, and digested on a water-bath for five or six hours. During extraction in the percolator the original blue colour gradually changed to a dark green.

The extract was evaporated to dryness in a platinum dish over a water-bath, the dried extract weighed 0·171 grm. or 26·45 per cent on the above, or 0·268 per cent on the original coral; hence the acetic acid extracts a larger proportion of matter than alcohol, but the amount of pigment dissolved may not be proportionately greater; the residue was dark green in colour, with a resinous appearance, closely adherent to the dish, without blisters, and somewhat deliquescent.

On heating, the residue melted and assumed purple, blue, and other iridescent tints; it also gave off a disagreeable nitrogenous odour like burnt fish, similar to that from the crude pigment set free by hydrochloric acid and by the alcoholic extract; dense white inflammable fumes were also emitted.

The fixed residue or ash was of a brownish colour, and weighed 0·123 grm., equal to 1·90 per cent. It was found to consist principally of iron, phosphoric oxide, lime, and magnesia. Hence the acetic acid extracts more organic matter, and less ash or mineral matter.

No traces of crystal form could be detected even under the microscope in any of the residues left by the acetic acid solutions.

On evaporating the glacial acetic acid solution of the pigment to dryness over a water-bath and taking up with hot glacial acetic acid a second time, the solution was of a light brown colour instead of blue. The ash from this brown extract also contained iron and phosphoric acid.

When solutions of the coral blue and of indigo in acetic acid are compared side by side, the former is seen to be brighter, and to have a green shade as compared with the indigo blue. The colour is between that of indigo and copper sulphate solution.

When a luminous flame is viewed through it the flame appears of a bluish-green, but when viewed through sulphindigotic acid, or indigo in acetic acid, the flame is more or less reddish-purple.

The spectrum of the coral blue in glacial acetic, formic, and lactic acids, and alcohol, is mainly blue and green, a little of the extreme red is visible and some of the yellow, but the bands are by no means well defined.

Solutions in glacial acetic acid when diluted gradually fade, and a voluminous whitish flocculent precipitate of organic matter is formed, which on ignition burns with a nitrogenous odour.

The undiluted solutions in glacial acetic, in strong formic and propionic acids, faded very slowly, and did not become turbid even after standing six months. The strong solutions of the pigment when exposed to the light do not fade so quickly as those of sulphindigotic acid and of indigo in glacial acetic acid. To test this, solutions of equal depth of colour were made, and left exposed to diffused daylight; the indigo solutions faded and lost the blue tint in a day or two, and after a week or two became practically colourless, while the coral blue solution had faded but slightly. A faded solution of indigo in glacial acetic acid is quite red (salmon colour) by gaslight.

The alcoholic solution fades more quickly than the acetic and formic acid solution, and especially when diluted; a fluocculent precipitate is gradually formed, and the solution turns brown; finally, after two or three weeks, it becomes colourless.

The best solvents for the pigment were found to be formic acid, hot glacial acetic and lactic acids, and absolute alcohol.

The acetic acid solution does nor dye wool, silk, or cotton, neither is it fixed by alum or ammonia.

It yields a very pale bluish-lake with alum and ammonia, but the colour fades in a few days. It also yields precipitates with baryta and lime waters, also with lead acetate; these precipitates require further examination.

Action of Reagents.

1. *Alcohols and their Derivatives.*—The crude pigment set free by hydrochloric acid is insoluble in methyl alcohol, also in ordinary alcohol, although soluble in absolute alcohol; it is insoluble in cold amyl alcohol, but on boiling it yields a dull greenish coloured solution. It is also insoluble in amyl acetate. It is insoluble in ether, ethyl acetate, and chloroform; also in acetic anhydride, although glacial acetic acid is one of its best solvents.

When boiled with dichloracetic acid it yields a pale green solution, with monobromacetic acid it yields a pale grass-green solution changing to a greenish-brown on boiling.

It is insoluble in oil of winter-green (methyl salicylate).

It is but slightly soluble in aldehyde, in paraldehyde, and in acetone. It is insoluble in glycol; with glycerol it gives a pale greenish solution which quickly fades; it also imparts a pale green colour to hot dichlorhydrin.

2. *Hydrocarbons.*—It is not dissolved by kerosene, naphtha, nor by the pure paraffins, neither is it soluble in such olefines as caprylene and octylene; the latter, however, acquires a slight green tint when heated with the pigment.

With eucalyptus oil it yields a pale green solution, and leaves a greyish gelatinous-looking residue of proteid matter, many times the volume of the original pigment, with black specks of the colouring matter embedded in it.

It does not yield a coloured solution with turpentine, either hot or cold, but after standing in it for some weeks the turpentine lost its original pale straw coloured tint, and became viscid, the pigment also lost its colour, and left a grey residue or skeleton.

3. *Acids.*—With nitric acid the pigment gives a yellow or orange coloured solution fading to yellow, probably due to the formation of picric acid. The colour is not restored by alkalis.

It has already been stated that the pigment is insoluble in hydrochloric acid.

It is insoluble in dilute sulphuric acid, 1 to 4 aq., but with concentrated sulphuric acid it gives a greenish coloured solution in the cold; on boiling the colour darkens, and on filtering through glass-wool an almost black liquid is obtained; on dilution a dusky blue filtrate passes through, but on standing, a black precipitate forms, and the solution becomes colourless; this black precipitate gives a blue solution with acetic acid, so that the pigment is sufficiently stable to resist the action of hot sulphuric acid.

Organic Acids.—Formic acid dissolves it readily both hot and cold to a beautiful blue colour similar to that yielded to acetic acid; on evaporating to dryness over a water-bath it leaves a greenish coloured residue, and this on ignition chars in much the same way as the acetic residue, and leaves a ferruginous-looking ash.

The residue insoluble in acetic acid, and the other above-mentioned solvents after repeated treatment, until the solvent no longer became coloured, is practically black. On heating this residue on platinum it burns slowly without flame, emits a nitrogenous odour, and leaves a considerable amount of ash, which is of a ferruginous colour, and appears to have much the same composition as that from the crude pigment itself.

Propionic Acid.—Slightly soluble in the cold; when

boiled it yields a bright blue solution equal to that in glacial acetic acid, and as permanent.

Propionitril.—Insoluble.

Butyric Acid.—Insoluble in the cold, but yields a pale greenish solution when boiled. *Isobutyric Acid* takes up a little of the blue on warming.

Heptoic, Caprylic, and Nonylic Acids.—Insoluble.

Lactic Acid.—(Ethylidene lactic acid).—Slightly soluble in the cold, but when warmed the solution is a full bright blue, as good as the acetic acid solution. The black residue insoluble in lactic acid imparts no colour to acetic acid. On concentrating the lactic acid solution over the water-bath, the colour gradually fades, and acquires a light brownish tint.

Glycollic Acid.—Gives light green solution, a little darker on warming.

Oleic Acid.—Insoluble, on boiling the acid becomes brown.

Tartaric Acid.—A faint blue colour on boiling.

Oxalic Acid.—Insoluble.

Citric Acid.—Yields a pale blue solution on boiling.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

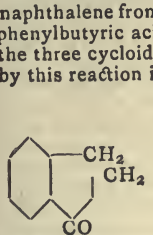
Ordinary Meeting, June 15th, 1899.

Professor T. E. THORPE, F.R.S., President, in the Chair.

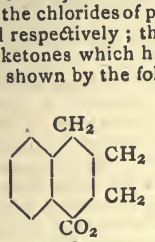
(Concluded from p. 18).

100. "*Synthesis of Phenoketoheptamethylene.*" By F. STANLEY KIPPING, D.Sc., F.R.S., and Miss L. HALL.

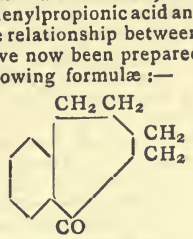
In continuation of previous work on the formation of cycloid ketones (*Trans.*, 1894, lxv., 480; 1899, lxxv., 144), the authors have studied the action of aluminium chloride on phenylvaleric chloride, $Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$, and find that, under suitable conditions, the reaction proceeds in accordance with the equation: $Ph{\cdot}[CH_2]_4{\cdot}COCl = HCl + C_{11}H_{12}O$. The product is a ketone, and is in all probability a phenoketoheptamethylene (or phenoheptaphanone) produced by an intramolecular condensation exactly analogous to that which occurs in the formation of α-hydrindone and α-ketotetrahydronaphthalene from the chlorides of phenylpropionic acid and phenylbutyric acid respectively; the relationship between the three cycloid ketones which have now been prepared by this reaction is shown by the following formulæ:—



α-Hydrindone.



α-Ketotetrahydronaphthalene.



Phenoketoheptamethylene.

Phenoketoheptamethylene is a colourless liquid having an odour very like that of peppermint; it is volatile in steam and only very sparingly soluble in water. *Phenoketoheptamethylene semicarbazone*, prepared in the usual manner, crystallises in glistening plates melting at about 219°; it is decomposed by dilute sulphuric acid, the ketone being regenerated. The analysis of this compound gave C = 66·4, H = 7·2, the numbers demanded by theory for $C_{12}H_{15}N_3O$ being C = 66·4, H 6·9 per cent. As the new ketone contains a closed chain of seven carbon atoms attached to the benzene nucleus, and is the first compound of this kind which has been obtained, the authors are making further experiments to confirm their views as to its constitution, and are also investigating its derivatives.

101. "*Organic Compounds containing Silicon.*" By F. STANLEY KIPPING, D.Sc., F.R.S., and LORENZO L. LLOYD.

Since the publication of various papers by Polis (*Ber.*, 1885, xviii., 1542; 1886, xix., 1012, 1024), very little work has been done on organic compounds containing silicon, more especially as regards those of the aromatic series; the authors, having recently taken up the study of some compounds of this kind, desire to record briefly a few of their results. In the preparation of silicon tetraphenyl by the method described by Polis (*loc. cit.*), a by-product melting at 148° is usually obtained in small quantities; this substance is triphenylsilicol, $(C_6H_5)_3Si{\cdot}OH$, and is doubtless identical with the compound obtained by Polis by decomposing triphenylsilicon chloride with water, in spite of the fact that the melting point assigned to it by Polis is only 139—141°. Triphenylsilicol crystallises in large transparent prisms, and when boiled with acetic chloride it is converted into *triphenylsilicyl acetate*, $(C_6H_5)_3Si{\cdot}OAc$; the last-named compound forms colourless prisms and melts at 91—92°.

When triphenylsilicol is dissolved in glacial acetic acid, and the solution warmed with a little concentrated nitric acid, a colourless, crystalline substance is gradually deposited; this product gave on analysis results agreeing with those required for *triphenylsilicyl ether*, $(C_6H_5)_3Si{\cdot}O{\cdot}Si(C_6H_5)_3$, and as it is also produced by the action of other mineral acids on the alcohol, there is little doubt as to its having this constitution. Triphenylsilicyl ether crystallises from acetic acid in colourless plates and melts at about 221°.

It has also been found that silicon tetrethyl (silicononane) (which was prepared long ago by Friedel and Crafts from silicon tetrachloride and zinc ethyl) can be obtained by treating a mixture of silicon tetrachloride and ethyl bromide with sodium; this method of preparation being a comparatively easy one, the investigation of silicon tetrethyl and its derivatives is also being continued. The estimation of the silicon in many of those silicon compounds which volatilise without decomposition is best carried out by heating in a crucible with concentrated sulphuric acid and weighing the residual silica; although this method may not be so generally applicable as that suggested by Polis (*Ber.*, 1886, xix., 1024), it gives very good results in many cases, and is very easily carried out.

102. "*The Velocity of Reaction before complete Equilibrium.*" By MEYER WILDERMAN, B.Sc., Ph.D.

The reactions investigated were the solidification of supercooled liquids and solutions, the separation of the solid from the pure liquid solvent and from its solutions (*e.g.*, velocity of ice separating from pure water and from solutions of various salts), the separation of dissolved substance from supersaturated solutions, the melting of pure solid solvent in the warmer liquid solvent and in solutions, &c. The reactions take place very quickly, some of them lasting only 15 seconds. Advantage was taken of the fact that the above reactions were accompanied by an evolution or an absorption of heat, which is directly proportional to the amount of ice or salt separated. The velocity of ice separation was determined by the rate of change of temperature in the system. A platinum thermometer was used and the deflections of the galvanometer were photographed on a revolving drum. The author finds that the following general equation holds good for all the above reactions,—

$$\frac{dt}{dz} = C\,(t_0 - t)\,(t - t_{ov} + K),$$

where t_0 is the temperature of equilibrium, t_{vo} that at which the reaction is started, K an instability constant. In other words, the velocity of reaction at the time z is directly proportional to the remoteness from the state of equilibrium, to the surface of contact of the two reacting parts of the heterogeneous system, and to the instability constant K. Hence a supercooled liquid or supersaturated solution must spontaneously crystallise when a certain

limit, indicated by K, is passed. From the above equation, it follows that complete equilibrium is "static," whilst incomplete equilibrium is "dynamic."

103. "*The Ultraviolet Absorption Spectra of Albumenoids in relation to that of Tyrosin.*" By A. WYNTER BLYTH.

The author has studied the ultraviolet absorption spectra of egg-albumin, serum, albumin, legumin, casein, Schrotter's albumose, certain toxalbumins, and tyrosin. He comes to the conclusion that the absorption band of ordinary albumin is identical with that of tyrosin. Gelatin, Schrotter's albumose, and certain other albumenoid substances show no band; in these, tyrosin is absent. The author describes a special cell facilitating the study of absorption spectra. A solid block of quartz is cut into steps, the faces of the steps and the back of the quartz being highly polished; the cell is completed by a quartz plate and glass ends; in this way, with one filling, successive thicknesses may be brought before the slit.

104. "*An Explanation of the Laws which Govern Substitution in the case of Benzenoid Compounds.*" (Third Notice). By HENRY E. ARMSTRONG.

This subject was dealt with somewhat fully in two communications made to the Society in 1887 (*Trans.*, li., 258, 583). It was then suggested that the formation mainly of meta-di-derivatives from mono-derivatives containing acidic radicles is perhaps due to the production, in the first instance, of a compound in which the acting molecule is associated with the acidic radicle. The object of the present note is to unreservedly withdraw this hypothesis, and to substitute what is believed to be a rational explanation, which has been arrived at after prolonged study of the subject with the assistance especially of Messrs. Berry and Lewis.

Owing to the readiness with which aniline is acted on by various agents, a false idea has been engendered as to the influence of nitrogen on substitution: in reality, it has a very slight predisposing power. Thus, although azobenzene readily forms an unstable perbromide, it is brominated only with difficulty, and is not easily acted on by substituting agents generally. Diazobenzene perbromide and the diazosulphonate from sulphanilic acid manifest complete indifference to bromine. In point of fact, there is little doubt that the activity of aniline and similar amines is the outcome of the presence of hydrogen in the amino-group; and it is even probable—as suggested in the second of these notices—that the formation of ortho- and para-compounds from primary and secondary amines is always preceded by that of the related compound in which hydrogen in the amino-group is displaced. A similar argument is applicable to the phenols, but there is little direct evidence of any prior displacement of the hydrogen of the hydroxyl group. In any case, in the formation of both ortho- and para-compounds from amines and phenols, there is reason to suppose that nitrogen and oxygen respectively act as attractive and also as orienting elements.

On the other hand, when meta-compounds are formed from amino-derivatives, probably it is because the nitrogen is so situated as to be both destitute of attracting power and possessed of ortho- and para- inhibiting power. Evidence of such inhibiting power is afforded by Miss Evans's observation (*Proc.*, 1895, xi., 235; 1896, xii., 234) that when subjected to the action of bromine, dimethylanilineparasulphonic acid yields a mono-derivative which is stable in presence even of a large excess of bromine at ordinary temperatures—a behaviour altogether different from that of anilineparasulphonic acid, which is at once converted into tribromaniline on merely adding bromine to its aqueous solution.

When negative acid radicles are introduced into the amino-group of aniline, a far greater effect is produced than by positive radicles. Thus, when acetysulphanilic acid is acted on by a single molecular proportion of bromine, at least 50 per cent of parabromacetanilide is produced, and the monobrominated acid which is simultaneously formed yields practically nothing but dibromacetanilide when acted on by bromine. The behaviour of benzoysulphanilic acid is similar to that of the acetyl acid.

An equally remarkable effect is produced by alkylating phenolparasulphonic acid. Whereas this acid is converted with extreme facility into the dibromosulphonate, and it is difficult to arrest the action at any earlier stage, the methoxy-, ethoxy-, and benzyloxy-acids prepared from it yield a large proportion of the monobromophenol *ether* together with monobrominated sulphonate when subjected to the action of only a single molecular proportion of bromine, and when further acted on the monobrominated sulphonates yield dibromophenol ethers. But different radicles produce markedly different effects, the benzylated sulphonate giving little besides the bromo-ether, whereas the methylated and ethylated sulphonate yield about equal proportions of bromo-ether and bromo-sulphonate. The corresponding metacresol derivatives behave in a precisely similar way.

Ortho- and para-nitrophenetosulphonates also directly exchange the sulphonic group for bromine, no trace of brominated acid being formed; the corresponding phenol acids yield first a bromonitro-acid, and then the dibromonitrophenol.

But phenyl itself apparently exercises the greatest influence when it takes the places of hydrogen in phenol, phenyl ether para-sulphonic acid, $Ph{\cdot}O{\cdot}C_6H_4{\cdot}SO_3H$, absorbing but a small proportion of bromine, and without the sulphonic group being displaced.

The difference between an alkylated phenol and phenol is therefore similar to that which obtains between dialkylated aniline and aniline, and at least as great: the introduction of a complex radicle in place of aminic or hydroxylic hydrogen, in fact, produces effects which have not been as yet sufficiently considered.

In order to produce meta-derivatives from amines, it is necessary to paralyse as far as possible the ordinary ortho-para-orienting influence of the amino-group, and to give opportunity for the attack to take place in the nucleus; abundant evidence has been obtained that this can be done in many cases. When acetanilide is acted upon by sulphonating agents, it is initially converted into acetylsulphamic acid, *i.e.*, *sulphamated*; but the sulphamic acid is very prone to undergo change into sulphonic acid, and readily changes into ortho- or para-sulphonic acid, according to the conditions: consequently there is little opportunity for the sulphamic acid to sulphonate, and only traces of meta-acid can be obtained. Sulphamated benzanilide is far more stable, however, and it is easy under appropriate conditions to obtain a large proportion of benzoylmetanilic acid by sulphonating benzanilide; but the action readily proceeds a stage further, the benzoyl also becoming sulphonated. Paracetoluide and orthacetoluide also readily yield acids in which the sulphonic group is meta- to the nitrogen when the conditions are so chosen as to sulphonate the sulphamate which is initially formed. Again, if parabromacetanilide be cautiously dissolved in strongly fuming acid, and the solution be poured on ice and the liquid boiled, a product rich in ortho-acid is obtained; but if the sulphonation be less carefully conducted, so as to give opportunity for all the sulphamate to sulphanate, pure meta-acid is eventually obtained. Both 2 : 4- and 2 : 6-dibromacetanilide give meta-acid with far greater facility, the sulphamate in these cases being very insensitive to change, so that the ortho-acid is obtained from the one and the para-acid from the other only by heating the sulphate of the amine at about 180°.

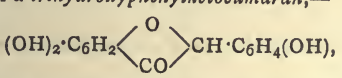
In the case of phenol, although when deprived of the company of hydrogen oxygen requires marked inhibitory powers, being destitute of basic properties, it cannot be rendered sufficiently unattractive to prevent its exercising ortho- and para-orienting power, consequently phenolic compounds do not yield meta-derivatives. But it is very noteworthy that 2 : 6-dibromophenetol is converted into a

polysulphonic acid with exceptional facility, just as dimethyl- and diethyl-aniline yield, the one a tetra-, the other a penta-derivative when brominated, although aniline yields only tribromaniline.

Briefly stated, the view now advocated is that in compounds which ordinarily furnish meta-di-derivatives, the radicle (NO_2, CO_2H, &c.), is not only unattractive and possessed of little or no ortho-para orienting power, but even exercises an inhibiting influence on these positions: consequently, when the two elements of any substituting agent become associated with positions 3 and 4 of the benzene nucleus, separation takes place from 4 rather than from 3, and therefore the meta-derivative is the chief product. The very numerous points of detail which require discussion will be dealt with in a paper in which the results alluded to in the course of this abstract and many others will be fully displayed.

105. "*The Colouring Matters of Dyer's Broom and Heather.*" By A. G. Perkin and F. G. Newbury.

The *Genista tinctoria* (dyer's broom), a yellow dyestuff formerly of some importance, contains two colouring matters, the first identical with the luteolin of weld (*Reseda luteola*), and the second, a new colouring matter, *genistein*. The latter has a composition corresponding to the formula $C_{14}H_{10}O_5$, colourless needles, and yields an acetyl derivative, $C_{14}H_7O_5(C_2H_3O)_3$, m. p. 197—201°, and a tetra-bromo-compound, $C_{14}H_6Br_4O_5$, colourless needles melting above 290°. On decomposition with alkali, it gives phloroglucinol and an acid of the formula $C_8H_8O_3$, m. p. 147—149°; this, with fused alkali, forms para-hydroxybenzoic acid, and appears to be *parahydroxyphenylacetic acid*. *Genistein dimethylether*, colourless leaflets, m. p. 137—139°, is insoluble in alkaline solutions, but forms a *monacetyl derivative* of the formula $C_{14}H_7O_3(OCH_3)_2{\cdot}Ac$, fine needles, m. p. 202—204°. A second product of the methylation, formed in minute quantity, melts at 187—189°, and appears to be isomeric with the above ether. In dyeing property, genistein closely resembles apigenin and vitexin, and to it the constitution of a *trihydroxyphenylketocumaran*,—



has been provisionally assigned. The colouring matter of *Calluna vulgaris* (heather) is quercetin, and there is also present a catechol-tannin in small quantity.

THE ROYAL INSTITUTION.

Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

At a General Monthly Meeting of the Members of the Royal Institution, held on the 3rd inst., Lord Kinnaird, Mr. A. F. Lindimann, and the Hon. W. J. Ward were elected Members. The Special Thanks of the Members were returned to Mr. Henry Vaughan for his donation of £20, and to Sir Henry Thompson, Bart., for his donation of £25 to the Fund for the Promotion of Experimental Research at Low Temperatures. The cordial thanks of the Members were returned to the Master and Wardens of the Merchant Taylors' Company; to the Lord Mayor and Lady Mayoress; to Dr. and Mrs. Mond; to Dr. and Mrs. Dewar; to Professor William Odling, and to the Teachers of Natural Science at Oxford, for their hospitality to the Members and guests of the Royal Institution during the recent Centenary Celebrations. The Managers reported that they had received gratifying assurances from their guests that the Centenary Celebrations, as a whole, were highly appreciated, and considered not unworthy of the past history of the Royal Institution, and of good augury for that new century of scientific work to which it has now to apply itself. Thus, Professor Cornu, on his return to Paris, reported to the French Academy of Sciences as follows:—

"La Royal Institution of Great Britain, fondée en 1799, par Benjamin Thompson, Comte de Rumford, fêtait les 5, 6 and 7 juin, le Centenaire de sa fondation; S. A. R. le Prince de Galles, Vice-Patron de l'Institution, a gracieusement demandé qu'on lui présentât nos confrères et leur a remis, dans l'une des séances commémoratives, le diplôme de membre honoraire de l'Institution Royale. Lord Rayleigh et M. James Dewar ont rappelé, dans deux remarquables Commemoration Lectures, les principales découvertes faites dans les laboratoires de l'Institution Royale, par Thomas Young, Sir Humphry Davy, Michael Faraday, John Tyndall.

"Les expériences les plus intéressantes ont été exécutées; en particulier, celles qui se rapportent à l'interférence des sons et à l'hydrogène liquide ont excité un véritable enthousiasme. Nous avons pu mesurer ainsi l'immense chemin parcouru depuis un siècle, grâce aux efforts déployés dans cette belle Institution.

"Enfin l'Université d'Oxford a convié tous les savants étrangers présents à Londres à visiter ses collèges, plus de cinq fois séculaires, qui renferment des richesses d'une valeur inestimable.

"Les deux Universités de Cambridge et d'Oxford ont témoigné à nos confières leur sentiments d'estime et confraternité scientifiques en leur conférant des titres de docteur honoraire.

"Nous rapportons donc de notre séjour parmi les savants anglais non seulement l'impression de la plus cordiale hospitalité, mais encore une véritable admiration pour la manière dont ils cultivent et honorent la science. L'histoire de ces Universités, et particulièrement celle de l'Institution Royale de la Grande-Bretagne, offre un example bien instructif: on voit par quelle méthode une nation, jalouse de s'élever au premier rang du progrès scientifique, d'encourager les recherches élevées et d'en faire comprendre les applications, parvient au but qu'elle s'est proposé.

"Elle choisit à chaque époque les savants les plus illustres, leur donne à la fois l'indépendance et les moyens matériels sans lesquels aujourd'hui on ne saurait réaliser de grandes découvertes.

"Il y a là un sujet de méditations et d'études pour ceux qui ont l'honneur de diriger le mouvement scientifique et qui s'efforcent de maintenir notre pays au rang élevé que ses traditions lui imposent."

It is satisfactory to be able to report that the Centenary Celebrations have not affected the pecuniary resources of the Royal Institution, as all expenses in connection therewith have been defrayed by private contributions. A balance remaining over of the sums contributed, amounting to £87, has been paid over to the Fund for the Promotion of Experimental Research.

NOTICES OF BOOKS.

A Treatise on Practical Chemistry and Qualitative Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By Frank Clowes, D.Sc. (Lond.). Seventh Edition. Pp. 516. London: J. and A. Churchill. 1899.

Beginning simply as a book for teaching practical chemistry to his own class, the author has so increased its scope that it is now offered to the public in the complete and extended form to which it has been gradually brought in the present seventh edition.

The book is divided into seven sections. The first six (omitting the fifth) contain a good practical course for senior students; the fifth is more especially for medical, pharmaceutical, and engineering students, and for those

who, preparing for some definite examination only, wish to become proficient in the analysis of a simple salt.

The seventh section deals with the fitting up and furnishing of laboratories, together with lists of apparatus, reagents, &c., which are required.

The present edition has been thoroughly revised and partly re-arranged and re-paragraphed, in order to facilitate reference. Several illustrations have been added, and important additions to the text have been made in the part dealing with organic chemistry. There is a very complete index of over sixteen pages.

Thirty-fifth Annual Report on Alkali, &c., Works. By The Chief Inspector. Proceedings during the Year 1898. London: Eyre and Spottiswoode. 1899.

As in 1897, we are sorry to see that the work of the inspectors was somewhat interrupted by illness and accident. The number of works now registered under the Acts in England, Ireland, and Wales is 1052. Of these only 86 are works decomposing salt. These numbers show a decrease of one alkali and five others since 1897. There are also 126 works registered in Scotland, of which a separate report is issued. During the year 1898, 4116 visits and 4562 tests were made.

There were, we are pleased to see, only two prosecutions under the Act. In the first, sulphuretted hydrogen was discovered to be escaping to the chimney of the works from the sulphate of ammonia process without any attempt being made to check it by temporary means, those in regular use being unavailable through the stoppage of other plant. The other prosecution was unimportant.

Very few complaints are now received of the escape of hydrochloric acid; the improvement in the plant, together with better technical knowledge, have naturally reduced the escapes of this gas, as well as of chlorine to a very low quantity.

The average escapes of acids of sulphur and nitrogen from exits in sulphuric acid works throughout the country show but little variation from former years.

Dr. Fryer draws attention on page 98 of this report to an improved packing for Glover towers; such results as are given will, if maintained, be of value to other manufacturers.

Very interesting results have been obtained this year in the study of processes for obtaining rectified sulphuric acid of high percentage monohydrate, and are recorded in the report to the Secretary for Scotland, pp. 132-8, on the Kessler process. It is understood that during 1899 a plant will be erected at the Government Works at Waltham Abbey.

To assist proprietors and managers of works scheduled under the Alkali Act, especially the smaller one, the Chief Inspector has, with the object of impressing upon the workpeople employed the responsibilities to which they are subject, suggested that copies of Section 25 of the Act of 1881 should be exposed in prominent positions; the section is here given in full on p. 31.

The individual reports of the different inspectors, giving full details of the work done in their own particular districts, complete the volume.

Practical Methods of Urine Analysis. For Chemists and Druggists. London: *The Chemist and Druggist.* 1899. Pp. 58.

This important subject is here dealt with in an able manner, and the information given and methods described are in every respect up to date. It will be found useful to the ordinary medical practitioner, as well as to the pharmaceutical chemist, who is often called upon to make such analyses. The descriptions are clear and the illustrations good.

CORRESPONDENCE.

QUADRIVALENCE OF OXYGEN.

To the Editor of the Chemical News.

Sir,—In a communication recently made to the Chemical Society by J. N. Collie, Ph.D., F.R.S., and Thomas Tickel, relative to the salts of dimethylpyrone, the authors have found it necessary, in order to explain some of their results, to assume the quadrivalence of oxygen. In connection with this matter they point out that J. F. Heyes advocated a similar view (*Phil. Mag.*, 1888) to explain, among other points, the difference between such peroxides as MnO_2 and BaO_2 on the one hand, and CO_2, SnO_2, &c., on the other hand; and, further, that Meldola had previously suggested that the oxygen atom in the azo-β-naphthols may be a quadrivalent, but they overlook my own earlier contribution to the subject—which was made to the British Association (Section B) at the Southampton meeting in 1882.

In my paper (see Chemical News, September 29, 1882) "On the Activity of Oxygen and Mode of Formation of Peroxide of Hydrogen," I then reviewed the modes of formation of peroxide of hydrogen and ozone, and argued that oxygen exhibits a variable valency, and must in some combinations be viewed as a tetrad.

I am not aware that anyone had previously represented oxygen as a tetrad, and although I am assured and believe that Dr. Collie and his coadjutor did not intentionally neglect a reference to my earlier contribution, I think that the matter is of sufficient importance to place this reclamation on record.—I am, &c.,

C. T. Kingzett.

Elmstead Knoll, Chislehurst,
July 11, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 25, June 19, 1899.

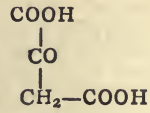
Research on the Vapours emitted by Two Varieties of Mercuric Iodide.—D. Gernez.—It has been known for a long time that mercuric iodide exists in two distinct crystalline forms—one crystallising in the rhombic form, of a red colour and stable at low temperatures; the other orthorhombic, yellow, and stable at high temperatures. The author investigates the conditions under which these two varieties are formed from their vapour. His experiments show that the vapour of mercuric iodide will form under the same conditions of temperature either of the two solid crystalline varieties, according to the nature of the nucleus of crystallisation which is in contact with the vapour.

Decomposition of Carbonic Oxide in presence of Metallic Oxides.—O. Boudouard.—In a previous paper the author has given the results of his researches on the decomposition of carbonic oxide by metallic oxides at temperatures of 445° and 650°. He now continues his researches to 800°. For these experiments the glass vessel used previously has to be replaced by porcelain. From the table of numbers obtained he deduces the result that the reaction of decomposition of carbonic oxide is a function of the time. The quantity of carbonic oxide formed increases in a regular manner, but, as at 650°, the decomposition of carbonic oxide is limited, the experiments show that the reaction stops when the gaseous mixture contains 7 per cent of CO_2 and 93 per cent of CO. It may also be remarked that the velocity of reaction is greater at 800°

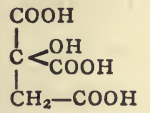
than at 650°. Whilst at 650° it is necessary to heat the tube for six hours to attain the limit, it is enough to heat it for two hours at 800°.

Decomposition of Carbonic Acid in presence of Carbon.—O. Boudouard.—The author has extended his researches on this subject to a temperature of 800°, the conditions of the experiment otherwise being exactly similar to those at the lower temperature. At this temperature the decomposition of carbonic acid is not total, but, as at 650°, the limit which is attained at 800° is the same as that found whilst investigating the decomposition of carbonic oxide (93 per cent of CO and 7 per cent of CO_2). At 925°.—Since the proportion of carbonic acid diminishes more and more in proportion as the temperature is raised, the author substitutes a gravimetric for a volumetric method. He finds that at 925° there still remains in the gaseous mixture resulting from the action of carbonic acid on carbon a proportion of 4 per cent of carbonic acid.

An Inferior Homologue of Citric Acid.—Augustin Durand.—Citric acid has been synthesised by Haller and Held, by acting on prussic acid with acetone dicarbonate of ethylene and transforming the product into citric acid by boiling with strong hydrochloric acid. The author has applied this method to the preparation of the homologues of citric acid by the action of HCN on the acetonic acids. Oxalacetic acid—



is transformed into—



an acid differing from citric acid by CH_2. The calcium salt of this acid crystallises with 5½ molecules of water. The zinc salt is formed as a white powder.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 4.

The Condensed Oxides of the Rare Earths.—G. Wyrouboff and A. Verneuil.—A very long paper, not suitable for abstraction.

The Complex Salts of Platinum; Oxalates and Nitrites.—M. Vèzes.—Already inserted.

The Symmetrical Dinitrodiphenylcarbamides.—H. Vittenet.—Up to the present only a few substituted diphenylcarbamides were known, such as the metadinitro-, the paradichloro-, and the paradibromo-diphenylcarbamides. The author thought it would be of interest to study and complete the series. For their preparation the general process of reacting on substituted aniline and its homologues was adopted. At the same time the action of the bases on the phenolic carbonates, and particularly on carbonate of phenyl, was also used. In this paper the authors describe successively the nitrocarbamides, the bases derived from them, and their stannic compounds; among these are dinitrodiphenylcarbamide 1 : 4, diamidodiphenylcarbamide 1 : 4, dinitrodiphenylcarbamide 1 : 3, diamidodiphenylcarbamide 1 : 3, dinitrodiphenylcarbamide 1 : 2, and diamidodiphenylcarbamide 1 : 2.

On Essence of Lemon-grass and Essenes of Citronel.—J. Flatau.—To decide whether perfectly pure citral would give a mixture of different semicarbazones, the author separated the terpenes which might be present with bisulphite of soda, and after three fractionations, he obtained a pure citral boiling at 119—121° at 22 m.m. The reaction of the semicarbazide with this citral gave crystals melting at from 140° to 155°. It is evidently a mixture of isomeric semicarbazones,

On the Ethers of Essence of Lemon-grass.—H. Labbé.—In a previous paper the author gave an analysis of lemon grass in which he mentioned a residue of 8 or 9 per cent which was not examined. This residue has an agreeable odour like that of the geraniol ethers; it was saponified with 5 per cent alcoholic potash, and in this manner by precipitating with water and washing with ether, an etherial solution containing terpenic alcohol and an aqueous solution were obtained. This solution, treated with hydrochloric acid, gives a precipitate of fatty acids which, extracted with ether, partially solidify at the ordinary temperature with the exception of a small quantity of oily acids. These acids dissolved in ammonia, and then treated with $BaCl_2$, give a yellowish white mass of impure salts. In boiling water these partially dissolve. The soluble portion deposits on cooling a white pulverulent mass, which, when dried in vacuo, proved to be a mixture consisting principally of caproic acid. The insoluble part was digested with ether, and decomposed with H_2SO_4. The acids taken up again by ether and converted into a barium salt gave a white powder, which, dried in vacuo, gave the following results:—Ba found, 25·08; the fusing point of the acid was 26—28°; theory requires for caprate of barium $(C_{10}H_{18}O_2)_2$; Ba = 28·3; the fusing point of capric acid is 31°. To completely identify these two acids the salt was decomposed, and a perfectly white acid obtained, melting at 30·5°. The barium salt prepared from this pure acid gave Ba = 27·9. Thus essence of lemon-grass contains 8 or 9 per cent of capric or caproïc ethers of an alcohol which is probably geraniol.

MISCELLANEOUS.

University College of North Wales.—Science Research Scholarship.—The Royal Commissioners for the Exhibition of 1851 have approved the nomination by the University College of North Wales of Mr. Robert Duncombe Abell to a Science Research Scholarship, of the value of £150 a year. Mr. Abell received his early education at Sandbach Grammar School, whence he proceeded in 1892 to the College, with a Cheshire County Council Scholarship, tenable in the Agricultural Department. After completing the two years' course for the College Diploma in Agriculture, he entered upon the B.Sc. course of the University of Wales, which he has just completed, taking first-class honours in chemistry. No honours of this grade have hitherto been awarded to any candidate in the faculty of science. Mr. Abell is about to enter the University of Leipzig, where he proposes to engage in a special research under the direction of Professor Wislicenus.

Leighton Buzzard Water Supply.—Colonel C. H. Luard, R.E., held a public inquiry on the 11th inst., on behalf of the Local Government Board, into an application of the Leighton Buzzard Urban District Council, to borrow £500 for the purpose of providing polarite filters upon the new system so successfully adopted by the Corporation of Hastings, the Southwold Waterworks Company, and other places. The Leighton water being obtained from the lower greensand, contains much iron in solution which requires oxidising and removing, and although the water is otherwise of high organic purity, yet its brown appearance has been a source of inconvenience and great complaint. In order to meet a widespread desire for a clearer drinking supply the Town Council decided to establish an efficient system of filtration, and after lengthened investigation and trials, eventually selected the polarite system of the International Syndicate as the most suitable and economical. The inspector, Colonel Luard, after taking the evidence of Mr. Phelan, the Council's engineer, to the above effect, had the polarite system explained by Mr. Frank Candy, of the International Purification Syndicate, and then proceeded to view the site selected for the filters.

Estimation of the Tartaric Acid in Raw Tartars.—Method adopted by the Chemische Fabrik at Winkel-am-Rhein.—For the estimation of total tartaric acid in wine lees and in raw tartars, the following method is recommended:—6 grms. of the finely powdered sample are placed in a 100 c.c. flask, and 9 c.c. of hydrochloric acid diluted to a density of 1·1 are added; this is left for about two hours at the ordinary temperature. The acid extract is then diluted to 100 c.c., well shaken, and filtered through a dry filter. 50 c.c. are then placed in a covered beaker, and 18 c.c. of a solution of carbonate potassium at 20 per cent is added; the whole is then heated until the precipitated carbonate of lime is properly deposited. This precipitate is filtered off, washed with boiling water, and the clear liquid evaporated down to about 15 c.c. in a porcelain crucible. After cooling, 3 c.c. of glacial acetic acid must be added, shake well, and let stand for the night. 100 c.c. of alcohol at 94—96 per cent must then be added while stirring; the precipitated tartaric acid is filtered, washed with alcohol, and finally dissolved in boiling water. The liquid may then be titrated with demi-normal potash. In the case of tartars, or tartrates of lime, 3 grms. of the sample should be taken and digested with 9 c.c. of hydrochloric acid. The solution is made up to 106·5 c.c., and 50 c.c. of this liquid taken for the estimation.—*Zeit. Anal. Chem.*, xxxvii., [5], p. 312.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2070

NOTE ON THE ELECTRO-DEPOSITION OF BRASS.

By T. J. BAKER and T. J. BAKER, Jun., B.Sc.

WHEN KCN is added to a solution of $CuSO_4$ in the cold, it is stated that the precipitate first produced is cupric cyanide (Valentin and also Roscoe), but that, on boiling, the precipitate loses $(CN)_2$ and becomes cuprous cyanide.

Both compounds are soluble in KCN solution, and the solution is in common use for copper plating and as a constituent of electro-brassing baths.

It was noticed that the weight of brass deposited from such a solution was frequently much in excess of that of the copper yielded from a copper sulphate solution placed in series with it.

Owing to the evolution of hydrogen during the deposition of the brass, no definite conclusion could be drawn from this observation.

It seemed of interest to examine the matter more carefully, and an apparatus was devised to allow of the collection of the hydrogen.

The cathode consisted of a thin sheet of platinum welded into a cylinder which exactly fitted over a wide glass tube, the latter serving to keep the platinum in shape and to prevent the deposition of brass inside the cathode. The anode was bent into a large cylinder concentric with the cathode. A graduated tube, closed at one end and fitted with a funnel at the other, was filled with solution and then inverted in the depositing vat exactly over the cathode. The volume of the hydrogen thus collected was reduced to 0° C. and 76 c.m., and the weight of cupric copper equivalent to it was calculated.

If c = weight of copper deposited from its cyanide solution,
z = ,, zinc deposited from its cyanide solution,
h = ,, hydrogen collected,
w = ,, copper deposited in the $CuSO_4$ cell.

Then, if the copper is deposited from its cyanide solution in the *cuprous* condition,—

$$w = \frac{c}{2} + \frac{63{\cdot}5}{65} z + 31{\cdot}75\, h.$$

In the table, the values of the right-hand member of this equation occupy the 4th column, and the values of w are placed in the 5th column.

I. The first experiments were made with a solution prepared by dissolving the precipitate due to the addition of Na_2CO_3 to 45 grms. $CuSO_4.5H_2O$ in 2 litres of water containing 60 grms. of KCN. This was prepared at a temperature of 13° C., and when used at that temperature gave the result stated in the first line of the table. When worked at 70° C., the result given on line 2 was obtained.

II. A zinc solution of the same concentration was then prepared in a similar manner, and at 12° C. yielded the result given on line 3.

III. Mixtures of the copper and zinc cyanide solutions were now made in various ratios, and all were worked at 65—70° C. The results were calculated as before, and are contained in the last section of the table.

When it is borne in mind that KCN solution exercises considerable solvent action on copper and zinc, and that each experiment lasted usually about half an hour, the small differences between the numbers in the last two columns are explained.

It may therefore be regarded as certain that the electrochemical equivalent of copper which is deposited from its cyanide solution, is always that of the metal in its *cuprous* state, and that this is also true when the copper is deposited in combination with zinc as brass.

Weight of deposit from cyanide solution.	Percentage of copper in this deposit.	Volume of hydrogen collected, in c.c.	Weight of cupric copper calculated as equivalent to the total foregoing deposit.	Weight of copper deposited from $CuSO_4$ solution in series with the cyanide solution.
		Copper Solution.		
0·024	100	67 6	0·203	0·197
0·591	100	26	0·369	0·402
		Zinc Solution.		
0·213	0	43	0·329	0·343
		Brassing Solution.		
0·319	84·6	65	0·356	0·397
0·537	83·1	15·3	0·354	0·382
0·474	70·2	10	0·33	0·345
0·316	46·8	24	0·3	0·332
0·369	34·4	15	0·339	0·374

Birmingham Municipal Technical School,
July, 1899.

A SIMPLE METHOD OF TITRATING THE AMMONIA IN THE WATERS FROM GAS PURIFIERS.

By M. LUBBERGER.

AT most gas-works the ammonia in the waters from the purifiers is estimated by means of a hydrometer; but this method is liable to error, as the presence of ammonia affects the density of the liquid in a very irregular manner. Another method consists in distilling the water from the purifier with lime, and titrating the distillate; but this method is too long.

In the year 1888 Knoblauch proposed a method consisting of adding lime to the liquor, diluted with five times its volume of water. After filtering, the liquor was titrated with normal acid. But in the presence of phenols part of the lime passes into solution, and, under these conditions, the titration gives very irregular results.

The ammonia dissolved in the gas-liquor is principally in the form of sulphide and carbonate. It can therefore be titrated directly with normal acid. The fixed ammonia, on the contrary, requires distilling in the presence of caustic lime, and as the proportion of this fixed ammonia is very small, the author is inclined to admit that the amount is constant for any particular gas-works always working under the same conditions. This hypothesis has been confirmed by a large number of analyses. The author, therefore, proposes to determine the quantity of fixed ammonia in about eight samples, taken at regular intervals spread over several weeks. The average found represents the proportion of fixed ammonia to be added to the results of the daily titrations. For titrating the free ammonia we proceed as follows:—

Three fragments of pure lime, about the size of a nut, are introduced into a flask of 400 c.c. capacity, which is half filled with the liquid to be titrated; the mixture must be shaken, and becomes of a reddish-brown colour. When all the lime is used up, the mixture is cooled, and 50 c.c. filtered off into a graduated flask. The filtered liquor is poured into a beaker, and titrated with demi-normal hydrochloric acid until the colour changes from brown to pale yellow. Of the total acid used we subtract the quantity necessary to saturate the lime in 50 c.c.; the remainder corresponds to the ammonia contained in the

liquor under examination. When operating on 50 c.c., 1 c.c. of demi-normal acid corresponds to 17 grms. of ammonia in 100,000 parts of liquor.

The solubility of the lime in the liquors in question is evidently variable according to the gas-works. It is therefore indispensable to determine it by a certain number of tests, and to take the mean of the results.—*Journ. f. Gasbeleucht.*, 1899, xlii., p. 1.

THE COLORIMETRIC ESTIMATION OF NICKEL.

By MAURICE LUCAS.

For some years past nickel has been used in proportions of from 1 to 3 per cent, to increase the tenacity of extra mild steel; the metal obtained, after tempering and annealing, has a very high limit of elasticity, and is not brittle. These properties have caused it to come into general use, notably in the manufacture of armour plates and of heavy guns, for which it is often used in conjunction with chromium.

For its rapid estimation I made use of the red colouration produced by sulphocarbonate of potassium or sulphocarbonate of ammonium with salts of nickel, a colouration which increases with the proportion of nickel present.

We obtain sulphocarbonate of ammonium by digesting freshly prepared sulphide of ammonium with one-twentieth part of its weight of sulphide of carbon, at a gentle heat for twenty-four hours; the sulphide of carbon is then separated by decantation.

Sulphocarbonate of potassium is prepared, according to Fresenius, by saturating one half of a 5 per cent solution of potash with sulphydric acid, adding the other half, and digesting at a gentle heat with one twenty-fifth of its volume of sulphide of carbon; the deep orange-red solution is separated from the undissolved sulphide of carbon. The deepest coloured of these two reagents is diluted with water so as to give them both the same intensity of colour, and they are then kept in well-stoppered bottles.

When added to a neutral or alkaline solution of a nickel salt they produce a red colouration which fades after a time, above all in the presence of alkaline salts, or on contact with the air.

To obtain these colourations uniform and durable it is necessary to use a large excess of the reagent, and, as this is also coloured red, there would at first sight appear to be some inconvenience.

In reality, however, we do not estimate smaller quantities of nickel than 2 m.grms., and that in a volume of 100 c.c.; we obtain the necessary colouration with 10 c.c. of the reagent, in which the intensity of colour does not correspond to more than one-tenth of a m.grm. of nickel, and as, on the other hand, the typical comparison tubes contain the same proportion, the inconvenience is reduced to simply a slight diminution of sensitiveness; with smaller quantities of nickel we can reduce the proportion of the reagent.

In this manner we make a scale of colourations corresponding to increasing quantities of nickel; each flask contains the same volume of liquid and about the same proportion of ammoniacal salts; care must be taken to keep them from contact with the air by corking them up tightly and using boiled water; the sulphocarbonate is not added until the solutions have been diluted to their proper volumes.

The salts of cobalt give a brown colouration under the same conditions; the process is only applicable after the separation of the two metals nickel and cobalt. This colouration is much more intense with sulphocarbonate of ammonium, which will serve to show the presence of cobalt with the nickel.

Copper gives in equal quantities a colouration almost as strong as that of nickel; we can, with sufficient accuracy, estimate it colorimetrically by means of ferrocyanide of potassium (*Bull. Soc. Chim.*, xix., p. 815), and subtract it from the quantity of Ni+Co found by means of the sulphocarbonate; but it is preferable to separate it first with sulphydric acid.

In the analysis of steels we attack ½ grm. of metal with aqua regia, and make two successive separations by ammonia and an ammoniacal salt. Dilute to 500 c.c., and take three separate quantities of this solution of 50 c.c. each; to the first add 10 c.c. of sulphocarbonate of ammonium; to the second, the same volume of sulphocarbonate of potassium. If the colouration is a deeper brown in the first than in the second, the nickel is mixed with cobalt, and their separation must be effected by any known method; but if not, the first is compared with the scale of coloured tubes, prepared by means of a titrated solution of nitrate of nickel containing 1 decigrm. of nickel per litre, taken originally from a much more concentrated solution verified by means of an electrolytic estimation. A salt of ammonia must be added to the comparison tubes.

The third portion of the ammoniacal liquid serves for a second test, profiting by the indications observed in the first case to take advantage of the most favourable conditions.

Finally, on driving off the ammonia, we must make certain that the solution gives no colouration with ferrocyanide of potassium which would indicate the presence of copper; if the latter is present, however, it can be estimated as has been shown above, or, better still, separated with sulphydric acid.

The accuracy of this method is of about one-tenth the proportion of nickel present.—*Bull. Soc. Chim.*, Series 3, xxi., No. 9.

NOTE ON PHOSPHATES.

By M. JULES JOFFRE.

In a previous paper I established the fact that the small coefficients of solubility of apatite and of tricalcic phosphate were not the same in pure water and in water charged with carbonic acid. Although these solubilities are extremely low, the differences observed should, however, have a greater or less influence on vegetation. In fact, as plants absorb and evaporate considerable quantities of water, it is only necessary for a body to be very slightly soluble for it to enter in appreciable quantities into the organism of plant life, and to produce a definite result on vegetation.

I have experimented with the white mustard plant, both in pure sand and in the same sand to which was added peat and carbonate of lime; and again by adding an excess of fertilising elements other than phosphoric acid.

The following are the results I obtained, the means of three successive sets of experiments. They are expressed by taking the weight of the yield without manure at 100, and comparing with this figure the weights obtained with the phosphates experimented on.

Experiments with pure sand:—

Without manure	100
Apatite from Logrosan	100
Tricalcic phosphate (bone-ash) ..	150
Gelatinous tricalcic phosphate ..	246
Monocalcic phosphate	321

Experiments made with a mixture of pure sand, peat, and carbonate of lime:—

Without manure	100
Apatite from Logrosan	112
Tricalcic phosphate (bone-ash) ..	142
Gelatinous tricalcic phosphate ..	197
Monocalcic phosphate	359

As can be seen, apatite (fluophosphate) produces only an uncertain and very slight effect.

The addition of tricalcic phosphate in the state of bone-ash produces, on the contrary, a very marked effect.

We can thus understand that, according as the materials called "phosphates" in commerce, and which are used in agriculture after simply being ground, contain either apatite, or fluophosphate, or tricalcic phosphate, the fertilising power will be very different.

The action of tricalcic phosphate is especially noticeable when it is used in the gelatinous state, that is to say directly after precipitation.

But in spite of the great differences in my results, I do not think we ought to consider these two sorts of tricalcic phosphate as being in different molecular states. The more complete dissemination obtained with the material in the gelatinous state is quite sufficient to explain the larger returns obtained.

Now if we compare all these results with those given by monocalcic phosphate—that is to say, with phosphate soluble in water—we see that there is an enormous difference in its action on vegetation. This phosphate produces results altogether superior, and more especially higher than those obtained with tricalcic phosphate in the gelatinous state, with which we get such excellent dissemination.

We must conclude from this, that it is not only because the monocalcic phosphate is better disseminated that the action is improved, but also because it is in nature absorbed by plants which are able to assimilate it, once it has entered into their organisms. The new experiments I have just made again prove the advantage there is in furnishing plants with phosphates soluble in water. —*Bull. Soc. Chim.*, Series 3, xxi., No. 10.

THE VOLATILISATION OF THE IRON CHLORIDES IN ANALYSIS, AND THE SEPARATION OF THE OXIDES OF IRON AND ALUMINUM.*

By F. A. GOOCH and FRANKE STUART HAVENS.

IT is well known that metallic iron is easily acted upon by an excess of chlorine at moderately elevated temperatures with the formation of ferric chloride, and that the product of the action of hydrochloric acid gas upon the metal is ferrous chloride. Out of contact with air, or moisture, both chlorides may be volatilised at appropriate temperatures—the ferric chloride below 200° C.; the ferrous chloride at a bright red heat. If water vapour, or oxygen, or air be present during the heating, both chlorides are partially decomposed with the formation of non-volatile residues, ferric oxide, or ferric oxychloride.

Analytical processes involving the volatilisation of iron at temperatures more or less elevated, in an atmosphere of chlorine or hydrochloric acid, have been the object of considerable attention. Thus Fresenius (*Zeitschr. für Anal. Chem.*, iv., 72), Drown and Shimer (*Journ. Inst. Min. Eng.*, viii., 513), and Watts (CHEM. NEWS, xlv., 279) have heated crude iron in chlorine to remove the metal and leave the non-volatile constituents; and Sainte-Claire Deville (*Ann. de Chim. et de Phys.* [iii.], xxxviii., 23) has employed hydrochloric acid to volatilise iron from mixtures of that metal with alumina—obtained by heating the mixed oxides of iron and aluminum in hydrogen according to Rivot (*Ann. de Chim. et de Phys.* [3], xxx., 188)—exposing the mixture, contained in a porcelain boat and placed within a porcelain tube, to the bright red heat of a charcoal furnace—an operation which was bettered by Cooke's (*Amer. Journ. of Science*, [2], xlii., 78) use of a tube of platinum instead of the porcelain tube and a gas blowpipe in place of the charcoal furnace. Sainte-Claire Deville (*Comptes Rend.*, lii., 1264) showed, further, that ferric oxide may be converted to ferric chloride and volatilised at the heat of the charcoal furnace if the current of hydrochloric acid is sufficiently rapid; but the curious effect was observed that in a sufficiently limited current of the acid no chloride whatever was volatilised, while the amorphous oxide was converted to the highly crystalline oxide of the same composition—a phenomenon which gave rise to a theory of the natural formation of specular iron in volcanic regions.

Quite recently, Moyer (*Journ. Amer. Chem. Soc.*, xviiii., 1029) has made record of an unsuccessful attempt (in the course of experimentation upon the volatility of certain chlorides at comparatively low temperatures) to convert ferric oxide completely to ferric chloride by the action of gaseous hydrochloric acid at about 200° C. At this temperature the greater part of the iron sublimed, but a residue remained, which, volatilising neither on long heating at 200° nor upon considerable elevation of the temperature, proved upon examination to be ferrous chloride. In the experiments to be described we have acted with gaseous hydrochloric acid upon ferric oxide made by igniting the nitrate prepared from pure iron deposited electrolytically by high currents passing between electrodes of platinum in a strong solution of ammonio-ferrous sulphate. The oxide, contained in a porcelain boat, was heated within a roomy glass tube over a small combustion furnace. The hydrochloric acid (generated by dropping sulphuric acid into a mixture of strong hydrochloric acid and salt, and dried by calcium chloride) entered one end of the tube and passed out at the other through a water-trap. In early experiments a high-reading thermometer was inserted through the stopper in the exit end of the tube so that its bulb was above and immediately adjacent to the boat carrying the oxide. In this way the actual temperatures of the vapours about the boat were fixed with considerable accuracy; later, after a little experience in gauging the effect of the burners, it was found that the temperatures could be regulated very closely without actually depending upon the thermometer.

We found, as did Moyer, that ferric oxide, submitted to the action of dry hydrochloric acid gas, volatilises partially as ferric chloride at low temperatures—180° to 200° C.—leaving ultimately a crystalline residue which does not change visibly when heated for an hour or two at 200°, or even at 500°, in the pure dry acid. According to our experience, this residue is generally slightly reddish or salmon-coloured; but sometimes, especially after a second heating, the boat having been withdrawn from the tube or exposed to the atmosphere (and so to moisture), the residue is white. When it is white it dissolves in water, yields the characteristic reaction for a ferrous salt with potassium ferricyanide, gives no reaction with potassium sulphocyanide, and upon treatment in weighed amount with potassium permanganate destroys the amount of that reagent theoretically required for its oxidation upon the supposition that it is ferrous chloride. The slightly coloured residue when treated with water yields a solution showing the reaction of a ferrous salt only, but when treated with hydrochloric acid, and then tested, shows the presence of a trace of iron in the ferric condition. Doubtless the colouration of the residue is due to an included trace of ferric oxide or oxychloride, which after exposure of the containing crystals to slight atmospheric action is more easily reached in the second heating by the gaseous acid. The amount of residue is somewhat variable, but approximates under the conditions of our work to from 5 to 10 per cent of the oxide taken; thus, in one typical experiment 0·1 grm. of ferric oxide left a residue which (withdrawn after cooling) weighed 0·0115 grm.

The greater portion of the ferric oxide volatilises when submitted to the action of the gaseous acid at 200° quickly and abundantly in the form of the greenish vapour of

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. vii., No. 41, May, 1899.

ferric chloride, and if the operation is interrupted at this stage the residue which remains is nearly black, insoluble in water, slightly soluble in cold hydrochloric acid, and readily soluble in hot hydrochloric acid with the formation of ferric chloride. It is probably something analogous to the oxychloride which Rousseau (*Compt. Rend.*, cxvi., 118), identifies as the product of the action of water upon ferric chloride at 275° to 300°. This dark residue yields to the action of the hydrochloric acid at 180° to 200° only slowly, but ultimately only the residue which is essentially ferrous chloride remains; thereafter little volatilisation occurs within the range of temperature of our experimentation—200° to 500°.

It is obvious that a reduction of iron in the ferric condition to iron in the ferrous condition takes place under the conditions of our work, and it is difficult to see how this can occur otherwise than by the direct dissociation of ferric chloride under the low partial pressure conditioned by the brisk current of hydrochloric acid gas. The temperature of formation, 180° to 200°, is far below that at which such dissociation is supposed to begin. Thus, Gruenewald and Meyer (*Ber. d. D. Chem. Gesell.*, xxi., 687), found, after cooling, no evidence or the dissociation of ferric chloride which had been heated in the Victor Meyer vapour-density apparatus to 448° in contact or partial mixture with nitrogen; but 10 per cent of the residue obtained by heating to 518° was in the ferrous condition. Friedel and Crafts (*Compt. Rend.*, cvii., 301), however, did see crystals of ferrous chloride at 440° on the walls of a Dumas container filled with the vapour of ferric chloride and nitrogen, the former exerting a partial pressure of 0·75; while ferric chloride volatilised into an atmosphere of chlorine without evidence of dissociation. It seems rather surprising, therefore, to find so large a percentage of dissociation as that shown in our experiments at a temperature so low—180° to 200°. Curiously, too, we find, on repeating the experiment of heating ferric oxide in gaseous hydrochloric acid, that if the temperature of the oxide is 450° to 500° when the brisk current of acid begins to act, the whole mass of oxide is converted and volatilises without residue. It is hardly to be supposed that the degree of dissociation at 450° to 500° can be less than that at 180° to 200°, and a test of the sublimate, after cooling, shows that it contains a ferrous salt. Plainly, ferrous chloride (formed by dissociation) has volatilised, and inasmuch as the ferrous chloride constituting the residue formed at 180° to 200° does not volatilise in the hydrochloric acid even at 500°, it is plain that the volatility of the former is not determined by the presence of the latter. Apparently, the cause of the completeness of volatilisation must be sought in its rapidity; and this is not an unreasonable hypothesis, if one considers that an action sufficiently rapid to keep above the boat an atmosphere of ferric chloride and its products of partial dissociation, might naturally provide the very condition which would be effective in counteracting the tendency of the residue to dissociate before it volatilises. If this hypothesis is correct, it is plain that the introduction of chlorine gas, the active product of dissociation, into the atmosphere of hydrochloric acid ought to bring about the volatilisation of the residue of ferrous chloride, formed at 180° to 200°, which refuses to volatilise in the acid alone. As a matter of fact, we find by experiment that if a little manganese dioxide is added to the contents of the generator, so that the hydrochloric acid may carry with it a little chlorine, every trace of ferric oxide is volatilised from the boat at 180° to 200°; and the residue of ferrous chloride found at 180° to 200° when the hydrochloric acid is used alone is likewise volatilised at the same temperature, when the admixture of chlorine is made.

These facts, that ferric oxide is completely volatile in hydrochloric acid gas applied at once at a temperature of 450° to 500° C., and at 180° to 200° if the acid carries a little chlorine, open the way to many analytical separations of iron from substances not volatile under these conditions. In the experiments of the following table we have applied these methods to the separation of intermixed iron and aluminum oxides. The ferric oxide employed was made, as before, by ignition of the nitrate prepared from iron deposited electrolytically by a strong current passing between platinum electrodes in a solution of ammonio-ferrous sulphate.* The aluminum oxide was made by igniting to a constant weight the carefully washed hydroxide precipitated by ammonia from a pure hydrous chloride thrown down from the solution of a commercially pure chloride by hydrochloric acid (*Am. Journ. Sci.*, ii., 346). The hydrochloric acid gas was made by dropping sulphuric acid into strong hydrochloric acid mixed with salt, and a little manganese dioxide was added when the mixture with chlorine was desired. The experimental details are given in the table.

Fe_2O_3 taken.	Al_2O_3 taken.	Al_2O_3 found.	Error.	Time.	Temperature.	Atmosphere.
Grm.	Grm.	Grm.	Grm.	Hours.	°C.	
0·1000	—	—	0·0000	½	450—500	HCl
0·2000	—	—	0·0000	1	,,	,,
0·1020	0·1015	0·1015	0·0000	½	,,	,,
0·2145	0·1006	0·1008	+0·0002	¾	,,	,,
0·1000	—	—	0·0000	¾	180—200	$HCl+Cl_2$
0·1000	0·1032	0·1032	0·0000	¾	,,	,,
0·1072	0·1013	0·1015	+0·0002	1	,,	,,
0·2045	0·1032	0·1033	+0·0001	1¼	,,	,,
0·1050	0·1023	0·1019	−0·0004	½	450—500	,,
0·2008	0·1007	0·1006	−0·0001	¾	,,	,,
—	0·1087	0·1087	0·0000	1	,,	,,

The residual alumina tested in several experiments by fusion with sodium carbonate, solution in hydrochloric acid, and addition of potassium sulphocyanide gave no indication of the presence of iron.

The separation of the iron is obviously complete at 450° to 500° when the mixed oxides are submitted at once to the action of hydrochloric acid gas, or at 180° to 200° when chlorine is mixed with the hydrochloric acid. Plainly, the extremely high temperatures employed by Deville are unnecessary if the mixed oxides are submitted at once to the action of hydrochloric acid at 450° to 500° without previous gentle heating in the acid atmosphere. We prefer, however, to use the mixture of chlorine and hydrochloric acid, not only because the temperature of the reaction is lower, but because it needs no regulation, while the danger of error arising from the liability of ferric chloride to dissociate, or from deficiency of oxidation in the oxide treated, or from mechanical loss due to too rapid volatilisation, is avoided.

THE PURIFICATION OF ACETYLENE.

By P. WOLFF.

The average composition of acetylene obtained by means of carbides of Swiss and of American manufacture is as follows :—

	American. Per cent.	Swiss. Per cent.
Acetylene	99 87	99·87
Phosphoretted hydrogen ..	0·04	0·02
Sulphuretted hydrogen.. ..	0·02	—
Ammonia	0·06	0·04

Carbides of recent manufacture give a gas which contains less sulphuretted hydrogen, and no trace of siliciuretted hydrogen. The quantity of sulphuretted

* The use of an anode of commercially pure iron wire naturally faci itates the operation, but in our experience the deposit thus obtained is likely to carry traces of impurity. In an attempt, too, to prepare pure ferric oxide from the oxalate thrown down out of ferrous sulphate with all precautions, the material obtained still held traces of silica, and possibly alumina, amounting to 0·0004 grm. in 0·1 grm. of the oxide.

hydrogen is always less when the generator contains a large excess of water. A judicious choice of raw materials enables us to reduce the amount of ammonia and phosphoretted hydrogen to a few hundredths per cent; but even such small quantities are still of serious inconvenience.

The method of purification proposed by Frank gives good results; it consists in using acid solutions of certain metallic salts, particularly chloride of copper. A part of the acetylene is transformed into aldehyde.

The author proposes the use of chloride of lime containing a small quantity of an alkaline chromate. The free chlorine is thus absorbed, and the acetylene does not undergo any decomposition.

Frank states that the acid solution of the metallic salt which he uses can be placed in an enamelled vessel, and that the quantity of aldehyde formed is very small. He claims that 1 litre of his solution will purify 14 cubic metres of acetylene, and that it can be regenerated by boiling, followed by aëration—*Journ. für Gasbeleuchtung*, xli., [42], p. 683.

THE MAXIMUM QUANTITY OF CHLORIDES CONTAINED IN SEA AIR.

By ARMAND GAUTIER.

I HAD occasion to estimate the chlorine in the air out in the open sea; this air was aspirated day and night at the lighthouse at Rochedouvres in the ocean itself, from the 22nd to the 25th October, 1898; the wind was west-north-west, and the weather fine and dry; the air passed slowly by aspiration through a long tube containing glass-wool previously washed and dried, and there deposited any matters that might be in suspension. I caused 341 litres of air at 16° to pass through this plug of glass-wool, under a pressure of 760 to 767 m.m. Carried to my laboratory this glass filter was washed with a little warm water, and the chlorides contained in the filtrate were estimated by means of a decinormal silver solution. A total quantity of 0·00462 grm. of chlorine was found, corresponding to 0·0076 of salt, which by calculation corresponds to 0·022 grm. of chloride of sodium per cubic metre of air.

For an average temperature of 15° this is the maximum; for we may mention that the lighthouse of Rochedouvres, where this air was aspirated, is about 50 or 60 kilometres from the coast, that a good breeze had been blowing for some days from the Atlantic, that half the air was collected during the night, and that although taken at about 9 metres above the level of the sea, it could not contain any of even the smallest particles of spray. This small quantity of salt, 0·022 grm. per litre of air, is thus the maximum. Nevertheless, it suffices perhaps with the traces of iodine which accompany it, to give to sea air the tonic qualities which characterise it.—*Bull. Soc. Chim.*, Series 3, xxi., No. 9.

Some New Diazoïc Primary Colouring Materials of the Benzene Series.—C. Bulow and H. Wolfs.—Following their research on the primary diazoïc colouring matters, the authors have examined those obtained by reacting with a diazoïc compound of the benzene series in acid solution, and then with a diazoïc compound of the naphthalene series in alkaline solution, or *vice versa*, on 3 : 1 oxydimethylaniline. To effect this they used, on the one hand, aniline, *o*- and *p*-toluidine, and *m*-xylidine, and on the other hand, α- and β-naphthylamine. The melting-points and the general appearance of the homologues or isomers of position do not appear to follow any particular rules; but the solution of these materials in sulphuric acid shows characteristic differences. A full account of the preparation and a description of these colouring materials will be found in the original paper.—*Berichte d. Deutsch. Chem. Gesell.*

THE BLUE PIGMENT IN CORAL (*HELIOPORA CŒRULEA*) AND OTHER ANIMAL ORGANISMS.*

By A. LIVERSIDGE, M.A., LL.D., F.R.S., Professor of Chemistry in the University of Sydney.

(Concluded from p. 31).

Action of Reagents (continued).

4. *Alkalis.*—In cold dilute ammonia it gives a pale blue solution which gradually fades in the course of a few weeks. It is much more soluble in strong ammonia, also in hot ammonia. On evaporating to dryness the residue is of a brownish colour.

It imparts a greenish colour to potash, both dilute and strong solutions, but when boiled with potash the solution turns brown. Moseley states that the colour is restored by acids, but I did not find this to be the case; a very faint dusky purple only was obtained. When boiled with ammonium, sodium, and potassium carbonates, it in each case yields a dingy slate-coloured solution with a slight purple tinge.

Aromatic Derivatives.—It is insoluble in benzene. Nitrobenzene is coloured green by it, but on heating this darkens and becomes brown. It also imparts a greenish tint to colourless phenol in the cold; on heating it yields a dark solution—the pigment does not, like indigo, appear to be re-deposited on cooling. On evaporating down to dryness over a water-bath and driving off the phenol, the pigment was left as a sap-green resinous-looking film, which under the microscope was seen to be made up of drop-like forms without any trace of crystallisation.

It appears to be insoluble in xylenol and also in aniline.

It is partly soluble in cresol (meta) to a dark green solution, and in cold creosote to a pale green; in hot creosote it yields a dark green solution similar to cresol.

The phenol, cresol, xylenol, aniline, and other similar solutions were filtered through glass-wool and evaporated, but none of them deposited the pigment in a crystalline form.

Salts.—It was found that the pigment is insoluble in sodium chloride and nitrate, both in the cold and when boiled. The acetate of sodium gave a slight shade of green, and the phosphate a hardly perceptible dusky purple tint. It is also insoluble in magnesium sulphate and stannous chloride. On boiling with stannic chloride, a bright blue solution is apparently obtained, but on filtering, most of the colour is left on the filter, and a very pale blue solution passes through.

Other Reagents.—No colour was imparted to olive oil, and the particles of pigment remained in it unbleached, although exposed to the light for some months, but the olive oil became quite colourless and viscid. It was found to be insoluble also in carbon disulphide, carbon tetrachloride, chloropicrin, thiophen, oil of cloves, cane-sugar solution, &c.

In all cases, although not always specifically stated, the reagent was used hot as well as cold, and in most instances the cold reagent was allowed to stand upon the pigment, with daily shakings for several weeks.

It is bleached by chlorine water (the colour is not restored by alkalis) and a greyish coloured residue is left (several other reagents left a similar residue); this residue or skeleton burns with a nitrogenous odour and leaves a considerable amount of ash—it apparently consists largely of the membrane of the pigment cells and perhaps cornein ($C_{30}H_{44}N_9O_{13}$). The ash is ferruginous in appearance, and contains iron, phosphoric oxide, lime, &c.

A mixture of glucose, ferrous sulphate, and lime does not appear to reduce it, as is the case with indigo.

The colour is discharged by nascent hydrogen (from zinc and hydrochloric acid) also by hydroxyl and sul-

* Read before the Royal Society of N. S. Wales, December 7, 1898.

phurous acid, and it is not restored by neutralising with an alkali.

After the above experiments were completed, the crude pigment was obtained by means of hydrochloric acid from the growing points of "live" coral, *i.e.*, coral which had been gathered while growing.

The tips or growing points were of a dull slaty-blue colour both externally and internally, and I expected them to yield a fuller blue than the "dead" coral, but the pigment obtained was of a pale chlorophyll-green tint, and its solutions in alcohol, glacial acetic and lactic acids were also of a pale green colour; it was practically insoluble in formic acid.

Under the microscope it was seen to be largely made up of membranous matter and cells containing granules of the green pigment. On exposure to light this green pigment gradually darkened somewhat.

Other Animal Blue Pigments.

The late Prof. H. N. Moseley gives an account of certain blue and other animal pigments in his paper on the colouring matter of various animals (*Quarterly Journ. Micro. Science*, xvii., 1877).

Purple Pentacrinin.—He states that many species of pentacrinins readily yield to acidified alcohol colouring matter with well defined spectra. The two principal bands correspond very nearly to those of turacin.

When rendered alkaline by ammonia the solution becomes bluish green. When the acid solution of pentacrinin is carefully concentrated it yields a dark violet amorphous precipitate, which is only slightly soluble in alcohol; it is not soluble in hydrochloric acid alone.

The fresh colouring matter is soluble in fresh water, but remains partly suspended, forming a slightly opaque dark purple solution; on acidifying it entirely dissolves to a beautiful pink; when this is rendered alkaline a green flocculent precipitate is thrown down.

Antedonin.—Antedonins are usually rose, orange, yellow, or brown colour to purple. A dark purple one was dredged off Cape York, Australia. The pigment was insoluble in glycerin, largely soluble in fresh water, and very soluble in weak spirit, and gave an intense fuchsine-coloured solution becoming pinker on dilution with alcohol.

When the alcoholic solution is rendered alkaline by ammonia, it changes to a deep violet, and a flocculent purple precipitate is formed, yielding a violet amorphous powder when dried, insoluble in alcohol and in oil of cloves.

A similar or the same colouring matter was yielded by a holothurian, from the South Indian Ocean; Moseley regarded it as identical with antedonin.

Land Planarians.—Two large species of *Rhynchodemus* were found at Parramatta, N.S.W., one red and the other Prussian blue. The blue is insoluble in alcohol, and becomes red on adding hydrochloric acid and is soluble in acidified alcohol.

Mollusca (*Aplysiopurpurin*).—A purple fluid is emitted by an *Aplysia* abundant on the shore of St. Vincent, Cape Verde; the purple fluid is soluble in alcohol. Said to contain aniline (see "Gmelin," vol. xviii., p. 422).

The purple colouring matter used by the ancients for dyeing linen and woollen, known as punicin, yielded by *Purpura capillus* and other mollusca, is a colourless secretion which becomes purple on exposure to light. It crystallises readily from its solution in aniline and is insoluble in alcohol and ether. Like indigo, it can also be crystallised by sublimation.

Doris.—A *Doris* had the surface of the foot coloured a dark purple; the pigment is soluble in alcohol acidified with hydrochloric acid. The spectrum resembles that from *Aplysia*.

Ianthinin.—The pigment of the purple fluid emitted by *Ianthina* was found to be soluble in spirit to a pale pinkish blue tint, and shows a brilliant red fluorescence, like æsculin, which is also blue by transmitted light. On adding a drop of hydrochloric acid the colour changes to a clear pale blue. The spectrum is well marked. The pigment is also soluble in glycerin, and yields a deep violet-coloured solution. The solution in ether resembles that in alcohol, but leaves a residue which dissolves in absolute alcohol to a blue solution. The ianthinin solutions all faded in a week or two.

Blue Stentorin.—Prof. E. Ray Lankester found that the blue pigment of *Stentor cæruleus* yields two well marked absorption bands in the spectrum, one in the red and the other in the green; also that it is unaffected by dilute acetic, hydrochloric, and sulphuric acids, while dilute potash intensifies it.

He also speaks in the same paper (*Quart. Journ. Micro. Science*, 1873, p. 142; and *Journ. of Anatomy and Physiology*, vol. iv.) of the blue pigment of *Velella* as being probably identical with that of other oceanic hydrozoa; no detached bands are exhibited, but the red and violet ends of the spectrum are cut off.

Fish.—Geo. Francis (Adelaide) describes a bluish green colouring matter from certain species of *Odax* common in St. Vincent's Gulf, S.A., giving a spectrum somewhat resembling that of chlorophyll (for figure and description see *Nature*, Dec. 30, 1875, p. 167). The pigment is soluble in water, rather bluer than chlorophyll; sulphuric acid precipitates it with albumen, but does not destroy the colour; it is bleached by light. The pigment is nitrogenous, and is destroyed by heat, chlorine, acetic acid, alkalis, ammonia, and alcohol.

Turacin (A. H. Church, *Phil. Trans. Roy. Soc.*, 1869, p. 627).—A blue pigment from the feathers of the turacoa or plantain-eater; it is soluble in water and contains copper.

Indigo.—Although essentially a vegetable production, it was specially tested for, since an indigo-forming substance occurs in both normal and morbid urine (for authorities see "Gmelin," vol. xviii., p. 407). But no certain indications of the presence of indigo were obtained from the coral pigment.

Pyocyanin.—Formed occasionally in pus. It forms blue acicular crystals arranged in crosses or rosettes. Melts on heating and does not sublime; soluble in water; reddened by acids, but the colour is restored by alkalis. Neither alcoholic nor the aqueous solution is precipitated by alum or lead acetate ("Gmelin," xviii., p. 415).

Hæmocyanin.—This is present in the blood of certain cephalopods, gasteropods, crustacea, and arachnida, and plays the same part as hæmoglobin in the blood of the vertebrates, *i.e.*, as a carrier of oxygen. It enters the gills colourless, absorbs oxygen and becomes blue; in its passage through the tissues it loses oxygen and again becomes colourless. Hæmocyanin contains copper in place of the iron in hæmoglobin. It coagulates at 65° and is precipitated by neutral salts and separated by dialysis (Haliburton, *Journ. Physiol.*, vi., 300).

Emu Egg Shell.—The dark green pigment of this shell gives a beautiful sapphire-blue to glacial acetic acid, also to formic and lactic acids. It is a still more beautiful colour than that from the coral.

Crustacea.—The blue pigment of the lobster and crab becomes red on boiling and by alcohol, but the coral blue does not.

It is unfortunate that so very little is known about the chemical composition of animal pigments, and this is especially the case with the non-crystallisable ones. In these notes I have only drawn attention to such of the animal pigments as appear to be at all allied to the blue coral pigment.

From the foregoing it will be seen that the blue pigment from this coral appears to differ more or less from all of the other animal blues referred to, including the bile pigments, but before it can be definitely stated to be a distinct substance, both this pigment and many of the others require to be further examined.

I am expecting to receive a further supply of the *Heliopora cærulea*, when I hope to be able to obtain the

pigment free from extraneous nitrogenous and other impurities. The pigment (or its accompanying impurities) apparently contains unoxidised sulphur.

THE PHYSIOLOGICAL EFFECT OF CREATIN AND CREATININ, AND THEIR VALUE AS NUTRIENTS.*

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Introduction.

The nitrogenous extractives, creatin and creatinin, are bodies the physiological importance of which should be determined. Creatin is a normal constituent of flesh, forming about 0·3 per cent of the total nitrogenous material of muscular tissue. It is one of the principal constituents of most meat extracts. The total amount of creatin in the human body may be taken to be something like 90 grms. Creatinin is a normal constituent of human urine. Opinions vary concerning the food value of creatin, creatinin, and other non-proteid amidic bodies. The opinion has often been advanced that such bodies may serve to protect protein, although they cannot serve to build tissue. If they protect protein, it would seem reasonable to suppose that they must yield energy in the body. The general question as to how far the non-proteid amidic substances, which occur most abundantly in foods of animal or vegetable origin, or as the first products of metabolism, are capable of undergoing oxidation in the human body, and thus contributing to the production of energy, is a subject on which more information seemed desirable. The usual methods of determining such bodies are not altogether satisfactory. Therefore, the investigations reported in this Bulletin were made, some studies of the chemical properties of flesh bases and the methods of separating them being necessary before the physiological work could be undertaken.

It has been found necessary to restrict the scope of the inquiry to the so-called flesh bases, creatin and creatinin. An abundant supply of asparagin and a considerable quantity of one or two other amidic compounds of vegetable origin have been procured, but these have not yet been worked with. In the case of asparagin, more has already been done by others in the line of experimenting proposed and less interest attaches to its relations to metabolism in the human body.

Such relations in the case of creatin and creatinin possess a double interest. On the one hand, creatin is a constituent of flesh food, and it is desirable to know whether and to what extent it becomes the material for metabolic change, and thus contributes to the production of energy. On the other hand, the same substance is formed from proteid metabolism in our own muscles, and to a much smaller extent in nervous and other tissues, and it becomes a question of importance what becomes of this creatin, and in what form is it eliminated. There is no reason to believe that creatin or creatinin can be utilised as synthetic material for the building up of the proteid tissues of the body. Creatin is easily changed into its anhydride, creatinin, and this latter substance is found habitually in the urine, so that it might be supposed to represent the slightly changed form in which both the creatin in food and that originating in the living muscles are eliminated. But the quantity of creatinin given off daily in the urine is in general quite small, and, although sufficient as a rule to account for the creatin of the flesh food consumed, the amount seems hardly large enough to cover also the creatin which may be supposed to originate in the living organism in the same time. Hence it has been suggested as probable that in some part of the body creatin may become converted into other and more complete cleavage products of metabolism, being in large part at least ultimately eliminated as urea. Should we, therefore, consider creatin and creatinin as representing nitrogenous material—received into the living body from without or formed in the body itself—which escapes further metabolism (save the mere conversion of one of these two closely related compounds into the other), and is simply excreted without contributing to the production of energy, or as representing an intermediate stage in the metabolism of protein which on further cleavage does in fact contribute something to the general output of energy of the body.

In connection with this latter hypothesis it may be noted that Stohmann and Langbein* found the molecular heat of combustion of creatin (anhydrous) to be 560 calories,† and that of urea to be 152·2 calories per grm. molecule. Supposing all the nitrogen of creatin to assume the form of urea, and neglecting any thermic result of the formation or oxidation of by-products, as two molecules of creatin will yield three molecules of urea, 331·1 calories will represent the heat evolved for each grm.-molecule of the former converted into and eliminated as the latter substance.

Views of Physiologists regarding the Rôle of Creatin and Creatinin.

The divergence and uncertainty of the views held on this subject by leading physiologists are indicated by the following condensed extracts from the works of well-known authorities :—

Thus, H. Newell Martin ("The Human Body," 1881, pp. 433—435) says :—

"In seeking antecedents of urea one naturally turns first to the muscles, which form by far the largest mass of proteid tissues in the body. Analysis shows that they always contain creatin, a body intermediate chemically between proteids and urea. The quantity of this in muscles is practically unaffected by work, and is from 0·2 to 0·4 per cent. Since it is readily soluble and dialysable, and, therefore, fitted to pass rapidly out of the muscles into the blood stream, it is a fair conclusion that a good deal of it is formed in the muscles daily, and carried off from them. Creatin, too, exists in the brain, and probably there and elsewhere in the nervous system is produced by chemical degradation of protoplasm; the spleen also contains a good deal of creatin, and so do many glands. This substance would therefore seem to be constantly produced in considerable quantities by the protoplasmic tissues generally; and since it belongs to a group of nitrogenous compounds which the body is unable to utilise for reconstruction into proteids it must be carried off. The urine, however, contains very little creatin or its immediate derivative, creatinin, and what it does contain depends mainly on the feeding, since it varies with the diet, and vanishes during starvation; so it is probable that this substance is converted into urea and excreted in that form. . . . While the urea resulting from further changes in the creatin formed in the tissues is a measure of the wear and tear of their protoplasm, part of the urea excreted probably has a different source; being due to the oxidation of proteids, as energy liberators or respiratory foods, before they have ever formed a tissue. When plenty of proteid food is taken the urea excretion is largely increased, and that very rapidly, within a couple of hours for example, and before we can well suppose the proteids consumed to have been built up into tissues, and these in turn broken down; in fact, there need be, and

* *Bulletin*, No. 66, United States Department of Agriculture, Office of Experiment Stations.

* Quoted in Beilstein's "Handbuch der organischen Chemie," 3rd ed., vol. i., p. 1189 See also article by Stohmann on "The Heat Equivalent of the Nutrients of Food," *Experiment Station Record* 6, p. 598.

† The results of new experiments which Professor Atwater has kindly made with his improved bomb calorimeter on the heat of combustion of both creatin and creatinin furnished by the writer are given further on.

usually is, under such circumstances, no sign of any special activity of any group of tissues such as one would expect to see if the urea always came from the breaking down of formed histological elements. . . . In artificial pancreatic digestions, when long carried on, two bodies, called leucin and tyrosin, are produced from proteids. It is found that when leucin is given to an animal in its food it reappears in the urine as urea; so the body can convert leucin into that substance. Hence, a possible source of some of the *luxus-consumption* urea is leucin produced during intestinal digestion; and this is very likely turned into urea in the liver. At any rate, the liver, to which the portal vein might carry all leucin thus formed, contains urea, which no other gland does; and when the liver is greatly altered, as in phosphorus poisoning and the disease known as acute yellow atrophy, urea almost entirely disappears from the urine. This latter fact seems to point to a final production of urea in the liver, whatever its immediate antecedents may be; whether muscle creatin, or intestinal leucin, or excess of peptones in the diet."

L. Landois ("A Text-book of Human Physiology," 1891, p. 505), summarises the subject as follows:—

"Although it is surmised that some of the nitrogenous bodies named above, more especially leucin, and perhaps also creatin, are the precursors of urea, yet we can not say definitely how or where the transformation takes place. Perhaps this is effected in the liver, and, it may be, also in the spleen."

The evidence in support of the theory that the liver is the seat of urea production is discussed further on.

Carl von Noorden's ("Lehrbuch der Pathologie des Stoffwechsels," 1893, pp. 70, 71) opinions are in effect as follows:—

"Creatin is undoubtedly a derivative of albumen. It is widely distributed in the body, principally in the muscular system, in which it is contained up to 0·3 per cent (O. Nasse). Creatin rarely comes under consideration as a final product of metabolism, since before its elimination it passes, probably in the kidneys, into its anhydride, creatinin. Only in case of alkaline reaction of the urine can a reverse change, into creatin, occur, in the bladder, or after discharge of the urine.

"The greatest part of the creatinin in the urine comes from the food, since the creatin of the food, easily absorbable from the alimentary canal, passes through the body unchanged, without being oxidised, and is, all of it, discharged as creatinin. He who eats much meat discharges much creatinin; hence it is found more abundantly in the urine of men, adults, and persons in health than in that of women, children, and sick persons; on the other hand, it either occurs in very small quantity or is altogether wanting in the urine of children fed only on milk (free from creatin). The average quantity discharged per day is about 1 grm. for an adult, healthy, and fully fed man; for a woman, 0·65 grm.

"A second portion of the creatinin of the urine comes from creatin which is formed in the body itself, probably in the muscle cells. Only this part is to be regarded as a product of the metabolism of albumen. The muscles contain, as has been mentioned, creatin in abundance; in the urine, apart from the creatin of the food, it occurs only in traces. Whether these traces represent the whole of the creatin metabolism in the muscles, whether in reality the quantity of creatin, as a whole, remains constant, and only these traces are worn off, is unknown. If the change in the stock on hand be a greater one it would have to be supposed that creatin is in the muscle itself converted into urea or other nitrogenous compounds, since leaving the muscle cell as creatin it could only appear unchanged in the urine. . . . Under conditions in which the muscular system of the body is rapidly consumed much creatin is eliminated." (See sections on "Starvation and Fever").

In a very recent treatise William H. Howell ("An American Text-book of Physiology," chapter on "Digestion and Nutrition," 1896, p. 279) says:—

"What becomes of the relatively large quantity of creatin in the muscles? It has been suggested that it is one of the precursors of urea; that it represents an end product of the proteid destroyed in muscle which is subsequently converted to urea in the liver or elsewhere. This supposition is supported by the fact that creatin may be decomposed readily in the laboratory, with the formation of urea among other products. But against this theory we have the important fact that creatin introduced into the blood is not converted into urea, but is eliminated as creatinin."

The subject is discussed at length by M. Foster ("A Text-book of Physiology," 1895, pp. 93, 590—595):—

"Urea does not arise in muscular substance itself as one of the immediate waste products of muscular substance.

"There is, however, always present in relatively considerable amount, on an average about 0·25 per cent of wet muscle, a remarkable body, *creatin*. This is in one sense a compound of urea: it may be split up into urea and sarcosin. This latter body is a methyl glycin; that is to say, a glycin in which methyl has been substituted for hydrogen, and glycin itself is amido-acetic acid, a compound of amidogen; that is, a representative of ammonia and acetic acid. Hence creatin contains urea, which has close relations with ammonia, together with another representative of ammonia, and a surplus of carbon and hydrogen arranged as a body belonging to the fatty acid series. . . . In dealing with the chemistry of muscle we saw that urea was conspicuous by its absence from the extract of muscle, whereas a very appreciable quantity of creatin was invariably present, and indeed was the prominent nitrogenous crystalline constituent of that extract. It seems difficult to resist the conclusion that creatin is the main normal nitrogenous product of the metabolism of skeletal muscles. If we accept this view, then upon the fact of the presence of creatin in, and the absence of urea from, the muscle itself, we may base the conclusion that while the muscle produces creatin as an antecedent of urea, the creatin so produced is converted into urea in some part of the body other than the muscle itself. . . . We must not, however, leave this statement without referring to a difficulty. Creatinin, as we have seen, is so frequently found in urine as to be regarded as a normal constituent, at all events of human urine; and creatinin is, as we have seen, the urinary form, so to speak, of creatin; the one body easily changes into the other by the assumption or removal of H_2O. This suggests the question: Is not the creatinin of urine the representative of the creatin of the muscles, which is thus excreted directly without undergoing the change into urea just discussed? In answer to this we may say in the first place that the quantity of creatinin in urine, though variable, is small; we may put the average at about 1 grm. in twenty-four hours. Now, muscle contains from 0·2 to 0·4 per cent of creatin; and this, taking the total muscle of the body (to say nothing of other sources of creatin which we shall mention presently) at about 30 kilos., would give 60 to 120 grms. creatin as present in the muscles of the body at any one moment. We can hardly suppose that the metabolism of muscle is so slow as out of this stock only to provide the 1 grm. of creatinin in twenty-four hours. Moreover, the creatinin in urine vanishes during starvation, is very markedly increased by a diet of flesh which contains creatin, and is not increased either by muscular exercise (which, however, would only indirectly affect the nitrogenous metabolism of muscle) or by such conditions—fever, for instance—as notably increase the urea of urine by increasing the nitrogenous metabolism of muscle. We infer, therefore, that the normal presence of creatinin in urine is due to the direct administration of creatin present in a (normal) flesh diet, and has nothing to do

with the muscular metabolism of the individual who is secreting the creatinin in his urine.

"The fact, however, that the creatin present in the muscle of the food and absorbed from the alimentary canal does not undergo a change into urea, but is excreted as creatinin—that is, virtually as creatin—warns us to be careful in adopting the conclusion arrived at above, that the creatin produced by muscular metabolism in the living body is a conspicuous antecedent of the urea of the urine. It is difficult to see why creatin passing into the blood of the capillaries of the muscle should be changed into urea, while that which passes into the capillaries of the portal system is not; for reasons which will be apparent presently we should rather expect that the latter, being more directly exposed to the influence of the liver, would be more readily and more completely converted than the former. Indeed, the question forces itself upon us: Is creatin, after all, the natural main product of the nitrogenous metabolism of muscle? Is it possible that in the normal metabolism of the living muscle the nitrogen leaves the muscular substance, and passes into the blood in another form, as some substance not creatin, and that it is as the muscle dies that creatin is formed, just as the solid myosin is unknown to the living fibre, but makes its appearance in a dying one? We have no positive evidence, however, that this is so, and meanwhile may continue to suppose that creatin is formed, and that in consequence creatin is a conspicuous antecedent of the urea of the urine; but we must not regard this as proved . . . we may probably consider the metabolism of the nervous system as a mere addition to that of the muscular system, at least as regards the point on which we are now dwelling. The amount of nitrogenous metabolism taking place in connective tissue, cartilage, bone, and the skin is probably still less. . . . The nitrogenous metabolism of the glands, however, more particularly that of the liver, does deserve special consideration . . . we have seen that pancreatic juice may carry part of the proteids on which it acts beyond the stage of albumose and peptone, and reduce that part into leucin, tyrosin, and other bodies. . . . We have seen reason to think that proteids of a meal are absorbed, not by the lacteals, but by the portal blood vessels, and such bodies as leucin probably take the same course. This being so, all these bodies pass through the liver and are subjected to such influences as may be exerted by the hepatic cells . . . we have, however, a convergence of evidence that the last stage of the process, namely the conversion into urea of some or other product of proteid metabolism which although allied to is not exactly urea, does occur in the liver. In the first place, a large quantity of urea seems to be present in the liver of mammals; in this respect the liver presents a strong contrast to the muscles. . . . In the second place, in certain cases of a form of disease of the liver known as acute yellow atrophy, in which the hepatic cells are so changed that their functional actively is largely diminished, the urea of the urine not only undergoes a very marked decrease, but appears to be replaced to a very large extent by leucin. This fact suggests that leucin (and not, for instance, creatin) is the chief immediate product of the nitrogenous metabolism of the body, and that the leucin thus produced is, in a normal state of things, converted into urea by the liver."

Previous Researches upon the Nutritive Value of Creatin and Creatinin.

There is but a small amount of direct experimental evidence as yet recorded bearing on the fate of creatin or creatinin introduced as such into the animal organism.

Ph. Munk (*Deut. Klinik*, 1862, p. 299), determined urea and creatinin in the urine of dogs when 2 grms. of creatin was injected into a vein, and under normal conditions. He concluded that the injection of the creatin increased (certainly) the amount of creatinin and (doubtfully) the amount of urea excreted. He did not determine whether any unaltered creatin was excreted. He also experimented to a very limited extent upon himself, taking by the mouth a rather small quantity of creatin, and reached similar results. Thus on a mixed diet he found in the urine when no creatin was taken 16 to 20·5 grms. urea, and 0·77 to 1·23 grms. creatinin; when 5·5 grms. creatin was taken, 21·8 grms. urea, and 1·48 grms. creatinin. The amount of urea reported seems remarkably low, assuming it to represent the excretion of twenty-four hours, and the increase in the amount of both urea and creatinin excreted is not great, while the creatinin represents but a small part of the creatin taken.

Meissner (*Ztschr. rat. Med.*, 1865, Series 3, xxiv., p. 100; 1866, xxvi., p. 225), also injected solutions of creatin and creatinin into the blood of dogs and rabbits. He found that creatin was eliminated with great rapidity by the kidneys. Creatinin at first passed unchanged into the urine, but afterwards seemed to undergo decomposition, no more creatin or creatinin being found. In the case of the dogs with a meat diet he found creatin as well as creatinin always present in the urine. Voit criticised these experiments in which the substances were injected into the blood on the ground that *time* enough for metabolism is not given. In support of this objection he cited the fact that a large amount of sugar can be fully disposed of when it has been swallowed, while a few grms. injected into the blood will appear unchanged in the urine.

Voit (*Ztschr. Biol.*, 1868, iv., p. 77), made some experiments with dogs, taking into account the quantity of creatin contained in the meat with which they were fed, and aimed at showing that, as more creatin (in the form of creatinin) was recovered from the urine than was given in the meat food, the surplus must have been formed in the living body. He came to the conclusion that in the breaking up of proteids in the muscles a certain part of the nitrogen takes the form of creatin, and is given off as such (or, rather, for the most part changed to creatinin) in the urine. He deemed it very improbable that creatin is changed into urea, the amount of creatin in the urine rising or falling in proportion to the amount taken in in flesh food plus the amount due to proteid metabolism in the muscles.

Voit also made some experiments on a dog, adding creatin and creatinin in separate form to the food. He concluded that creatin and creatinin are not changed to urea, of which there was no sensible increase, but that the greater part is removed in the urine, the failure to recover all being perhaps due to a part being held back in the alimentary canal in consequence of sparing solubility. He also reported that he found under the administration of creatinin the urine may become temporarily alkaline, creatin being then given off, formed from creatinin in the body of the animal experimented on.

It may be added that Max Rubner (*Ztschr. Biol.*, xx., p. 265), found by direct experiment on a dog with a respiration apparatus that the flesh bases of meat extract have no influence on the elimination of carbon dioxide or the production of heat.

It seemed, therefore, that experiments were desirable which might throw further light on this debatable question of the relations of creatin and creatinin to the chemistry of animal life.

(To be continued).

Action of Sulphide of Ammonium on the Nitrated Aromatic Nitramines and Nitrosamines.—J. Pinnow and P. R. Oesterreich.—The authors show that the *p*- and *o*-nitrophenylmethylnitrosamines are transformed by the action of sulphide of ammonium—with elimination of the nitro-group of the lateral chain—into nitromethylanilines, and the *o*-nitro *p*-tolylmethylnitramine into amidotolylmethylnitramine. When operating on the *p*-nitrophenylmethylnitrosamine, the nitroso-group is eliminated.—*Berichte der Deutsch. Chem. Gesell.*

ON A TEST, BY THE FREEZING-POINT METHOD, OF THE IONISATION COEFFICIENTS DETERMINED BY THE CONDUCTIVITY METHOD, FOR SOLUTIONS CONTAINING POTASSIUM AND SODIUM SULPHATES.*

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THE experiments described below were undertaken, at the suggestion of Prof. J. G. MacGregor, for the purpose of testing the values of the ionisation coefficients obtained by means of his graphical method (*Trans. N.S. Inst. Sci.*, 1895-6, ix., 101), in the case of a mixture of solutions of two electrolytes with a common ion, by employing them in the calculation of the depression of the freezing-point, and comparing the calculated values with values obtained by experiment.

The time at my disposal was very limited, and in consequence I was able to make the test only in the case of equimolecular solutions of two electrolytes. Potassium and sodium sulphates were selected as the electrolytes, not because of their being the most suitable for the purpose, but because I had been observing their conductivity and had already obtained some of the requisite data.

As, in determining the depression of the freezing-point, the solutions must be at a temperature of about 0° C., it was necessary that the ionisation coefficients should be determined for approximately the same temperature. Both the specific conductivities of simple solutions of the two electrolytes throughout the range of concentration of the simple solutions used in preparing the mixtures, and their equivalent conductivities at infinite dilution, had therefore to be determined for 0° C., as well as the depression of the freezing-point for the mixtures. In addition, in order to determine how closely the depression in the case of simple solutions can be calculated by means of ionisation coefficients determined by conductivity measurements, I observed the depression in the case of simple solutions also.

The work involved in making the desired test therefore included the following:—(1) The purification or testing of the materials; (2) the preparation and analysis of series of simple solutions and the preparation of the mixtures; (3) the measurement of the conductivity of series of simple solutions at 0° C.; (4) the determination of the equivalent conductivity at 0° C. of the two electrolytes at infinite dilution; (5) the calculation of the ionisation coefficients of the simple solutions; (6) the measurement of the depression of the freezing-point for the simple solutions; (7) the calculation of the depression for the simple solutions by means of the ionisation coefficients obtained from the conductivity measurements; (8) the measurement of the depression of the freezing-point in the case of the mixtures; (9) the determination of the ionisation coefficients of the electrolytes in the mixtures; and (10) the calculation of the depression of the freezing-point of the mixtures by means of these coefficients.

The Materials.

The salts were obtained as chemically pure from Eimer and Amend of New York, and were re-crystallised carefully three times, after which treatment no appreciable impurities could be detected.

The water used was purified by Hulett's method (*Journ. Phys. Chem.*, 1896, i., 91), except that a block tin condenser was employed instead of a platinum one. Portions of the distillate were treated in the same manner as to exposure to air, &c., as a solution would be, and their conductivity measured. It was found to vary from $0{\cdot}88 \times 10^{-10}$ to $0{\cdot}96 \times 10^{-10}$, expressed in terms of the conductivity of mercury at 0° C. It was kept in bottles which had been used for this purpose for several years.

Preparation and Analyses of Solutions.

The potassium sulphate solutions were prepared by adding to water a known weight of anhydrous salt which had been dried to constant weight in an air-bath, so as to form a known volume of solution at 18° C. In the case of the sodium sulphate, a solution was prepared, and analysed by gravimetric determination of the sulphuric acid present in a known volume of solution. Several solutions of both salts of different concentrations were prepared in the above manner, and others were prepared from these by addition of water, their concentrations being calculated. Check analyses were made whenever any portion had gone through two or three dilutions, and if found necessary the calculated concentrations were corrected from these results.

The complex solutions were prepared by mixing equal volumes of the constituent solutions at 18° C., the same precautions being observed for securing equality of volume of the constituents as are described in a former paper communicated to the Institute on the conductivity of these salts (*Trans. N. S. Inst. Sci.*, 1897-8, ix., 291).

The concentrations of the solutions at 18° C. would, of course, be slightly less than their concentrations at 0° C., but with solutions as dilute as those which I used, the difference could hardly affect the third significant figure.* I have therefore regarded the concentrations at the two temperatures as the same.

As the method of calculation required a knowledge of any appreciable change of volume which might occur on mixing, simple solutions of each of the salts were prepared, and density determinations were made of such solutions before and after mixing. These measurements were carried out at 18° C. with Oswald's form of Sprengel's pycnometer. They might be in error by about 5 in the fifth decimal place. No change of volume was found to occur on preparing the most concentrated mixture examined, which would appreciably affect its concentration with respect to the two electrolytes, when calculated on the assumption that no such change of volume occurred.

Method of Measuring Conductivity.

The method used was Kohlrauch's telephone method, and the apparatus was the same as described in the paper just referred to.

Two electrolytic cells were used, one for strong, the other for more dilute solutions. The first was U-shaped of the form shown by Ostwald in his "Physico-Chemical Measurements," p. 226, Fig. 178. The second was cylindrical, about 14 c.m. long, with an internal diameter of 3·3 c.m. It was provided with circular electrodes of stout platinum foil not easily bent. The stout wire supports of these electrodes were fused into glass tubes which passed through, and were sealed to, the ebonite cover of the cell. The electrodes were kept firmly in position by means of a rubber band passing over the cover and around the bottom of the cell. This cell being long and of the same diameter throughout, could, by variation of the distance between the electrodes, be used for solutions extending through a wide range of dilution.

The platinising of the electrodes was carried out as described in the paper cited above.

The water-bath described in the above paper was used for these experiments also, modified, however, when working at 0° C. as follows:—A cylindrical screen made

* From the *Transactions of the Nova Scotian Institute of Science*, vol. x., Session 1898-99.

* From Forch's observations on the thermal expansion of solutions of potassium sulphate (*Wied. Ann.*, 1895, lv., 100), and Marignac's on sodium sulphate (*Ann. Chim. Phys.*, 1871 (4), xxii., 385), I find that the difference of temperature referred to would affect the third significant figure of the concentrations only in the case of the stronger solutions examined, and in the case of these only to the extent of 1 or 2 units.—J. G. M.

of wire gauze about 15 c.m. in diameter was hung from a support so as to reach from the top, to within 6 or 8 c.m. of the bottom, of the bath. Inside this, the electrolytic cell containing the solution to be measured was placed, while outside was a mixture of snow and a very little sodium chloride. The screen thus prevented the snow from coming into contact with the cell, while the water around it could be thoroughly stirred. By varying the amount of salt the temperature could be kept within a twentieth of a degree of zero for half an hour at a time. An error of this amount in the determination of the temperature of the solution would cause an error of about 0·1 per cent in the determination of the resistance. The temperature of the room in which the observations were made was from 2° to 5° C. That one might be sure that the temperature of the solution to be measured had come to be that of the bath, measurements of the resistance were made at short intervals, and that reading taken which was found to be constant for successive intervals. The thermometer used was graduated to tenths of a degree centigrade, and could easily be read to twentieths. Its errors had recently been determined at the Physikalisch-Technische Reichsantalt, Berlin.

The factor for reducing the observed conductivities to mercury units was found by plotting observed conductivities at 18° C. against concentrations, reading off from these curves the conductivity values for concentrations examined by Kohlrauch, and comparing them with his results. The value thus obtained was found to be the same for each salt, and to be practically constant throughout the concentration range of my experiments. As the cell was of glass the reduction factor would not be appreciably different at 0° C. from what it was found to be at 18° C. To make sure that no change occurred in the position of the electrodes during the course of the experiments that would appreciably affect the reduction factor, every second or third solution was measured at 18° C. before reducing its temperature to 0° C., and the value of the conductivity obtained was compared with that previously obtained at the same temperature.

(To be continued).

NOTICES OF BOOKS.

An Introduction to the Carbon Compounds. By R. H. Adie, M.A., B.Sc. London: W. B. Clive, University Correspondence College Press. 1899. Pp. 90.

With the idea of enabling students to have a better grasp of physiological subjects, with regard to both animal and plant life, the author has endeavoured in this book to lead the reader to a consideration of the more important groups of carbon compounds, without laying too great stress on the general methods; the importance of understanding the chemical changes brought about by living matter cannot be overrated, and it must not be forgotten that the chemistry of organised matter is just as much a matter for experiment as is inorganic chemistry.

The course followed in this volume comprises the hydrocarbons, including the paraffin series, ethylene, acetylene, and benzene, the haloid derivatives, alcohols, ethers, aldehydes, sugars, acids, &c. The theoretical desciptions are followed by experiments which will help to impress the facts on the mind of the student.

Action of Ferric Chloride and Bromide on some Aromatic Carbides, and on their Halogen Substitution Derivatives.—V. Thomas.—In a previous paper the author published the beginning of this research. From the product of the action of ferric chloride on paradibromobenzene he now isolates two new bromotrichlorobenzenes, one of which melts at 93° with formula $C_6H_2Cl_3Br$, and the other melting at 138° and having the formula $C_6H_2Cl_3Br$.—*Comptes Rendus*, cxxviii., No 26.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, del'Académie des Sciences. Vol. cxxviii., No. 26, June 26, 1899.

Preparation of Fluorine by Electrolysis in a Copper Apparatus.—Henri Moissan.—Instead of using the expensive platinum apparatus hitherto employed, the author substitutes one of copper. Copper is less attacked by fluorine than most metals, owing to the fact that the copper becomes coated with a thin layer of copper fluoride. This substance is insoluble in hydrofluoric acid, and so prevents further action. The temperature must not be too low to prevent the union of the hydrofluoric acid and the alkaline fluoride from taking place throughout the whole mass. By means of this apparatus a continuous current of fluorine gas can be obtained.

Constitution of the Oxides of the Rare Earths.—G. Wyrouboff and A. Verneuil.—In a previous paper, the authors pointed out that no argument exists which is in favour of the hitherto accepted trivalence of cerium, lanthanum, and didymium, and the tetravalence of thorium. The investigation of the formation of various complex salts of cerium and thorium lead to the suggestion that the oxides of these two metals have the formulæ $(CeO)_3$ and $(ThO)_4$. In each case one of the CeO and ThO groups differ in function from the other two.

Preparation of Phenylic-chlorocarbonates.—E. Barral and Albert Morel.—The authors prepare these compounds by the action of a solution of carbonyl chloride in toluene on an aqueous solution of the sodium compound of phenols. The temperature at which the reaction takes place should not be allowed to exceed 40—50°; for above this temperature decomposition ensues and the symmetrical phenylic carbonate is produced.

Cerine and Friedeline.—C. Istrati and A. Ostrogovich.—The substance previously extracted from cork by one of the authors is subjected to fractional dissolution in, and crystallisation from, chloroform. By this means it is separated into two distinct compounds: cerine, $C_{27}H_{44}O_2$; and friedeline, $C_{43}H_{70}O_2$.

New Reactions of Indolic Bases and Albumenoid Compounds.—Julius Gnezda.—If indol or any of its derivatives are heated with excess of oxalic acid a purple colouration is produced. A similar reaction is given by albumen, peptones, and gelatin. Various other dibasic acids may be used instead of oxalic acids. Other colour reactions occur by means of hydrofluoric and hydrofluosilicic acids, which the author describes.

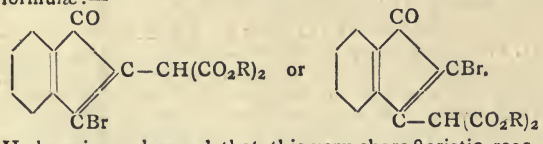
Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., November 28, 1898.

Action of Acetylene on Nitrate of Mercury.—K. A. Hofmann.—The author has recently announced that acetaldehyde furnishes with an aqueous solution of mercuric nitrate a white crystalline compound corresponding to the formula $C_2Hg_2NO_4H$. This compound has also been obtained by means of acetylene, which is a further proof of the transformation of this substance into acetaldehyde. The author finds that by reacting with acetylene on the warm solution of mercuric nitrate according to Erdmann's method, a mercuric compound of acetaldehyde or of vinoxylic alcohol is formed, which, after having been purified by means of dilute nitric acid, corresponds to the formula $C_2Hg_3NO_5H$, which can no doubt be developed as follows:—

$$\begin{matrix} NO_3Hg \\ OHg \end{matrix} \!\!> C - C \!<\!\! \begin{matrix} H \\ O \end{matrix}.$$

Action of Hydrate of Hydrazine on the Phenols.—L. Hoffmann.—During a research on the preparation of the derivatives of hydrazine containing phosphorus, the author found that the naphthols, under the action of hydrate of hydrazine, are transformed into naphthylhydrazines, and that in the same manner phenol gives, at a high temperature, small quantities of phenylhydrazine. With α-and β-naphthol the reaction takes place by heating with excess of hydrate of hydrazine for six hours to 160° in a sealed tube; it can be expressed by the equation $C_{10}H_7OH + NH_2.NH_2 = C_{10}H_7NH.NH_2 + H_2O$. With phenol it is necessary to heat up to 220°, but a small quantity only of phenylhydrazine only is formed.

Coloured Reactions of the Indones and Quinones with the Derivatives of Malonic Acid.—C. Liebermann.—It is well known that a coloured reaction takes place when the soda compound of malonic ether is made to react on dichlorindone. The author has now studied this reaction with dibromindone, and he found that a compound is formed corresponding to one of the following formulæ:—



He has since observed that this very characteristic reaction is susceptible of being generalised. Following this up, he has been led to examine the action of malonic ether on 2 : 3-dibrom-α-naphthoquinone, and he finds that it gives a magnificent blue colouration. The corresponding derivative of β-naphthoquinone gives a greenish blue colouration; the monobromo- and monochloro-β-naphthoquinone behave in an analogous manner. All these compounds are very unstable in alkaline solution. He has also observed that the soda compound of malonic ether acts on the non-substituted quinones. With α-naphthoquinone he obtained a bluish green, and with β-naphthoquinone a red solution. The fact that the same reaction is observed with the indones is interesting, inasmuch as it confirms the intimate relations which exist between the group of quinones and of the indones.

Some Derivatives of *o*-Tolunitrile.—W. Landsberger.—The author has studied the nitration of *o*-tolunitrile which gave 4-nitro-*o*-tolunitrile, fusing at 105°, of which the amide occurs in brilliant needles fusible at 173°, and the product of reduction, the amino-*o*-tolunitrile, in needles fusing at 88°. He also describes the chlorhydrate, the picrate, and the double salt of platinum. He further describes a research made on the action of the soda compounds of the methyl- and the ethyl-acetacetic ethers on the chloride of *o*-cyanbenzyl, and gives an account of the preparation and properties of several compounds.

Peracetylation of Phenacetine.—A. Bistrzycki and F. Ulffers.—One of the authors showed some time ago that the diacetanilide which forms on heating aniline with a large excess of acetic anhydride does not differ in its physiological properties from monoacetanilide (antifebrine). He has now repeated the experiment with phenetidine, of which the monoacetyl derivative (phenacetine) is a well-known medicine. The diacetphenetidide, which he prepared by heating phenacetine twice with a large excess of acetic anhydride, crystallises in ligroïn in colourless needles. Although but slightly soluble in cold water, it is more so than phenacetine. The diacetphenetidide appears, even in the smallest doses, to produce the same physiological effects as phenacetine; in equal doses it acts in a much stronger manner, but the effect does not last so long. The authors also describe another derivative of phenetidine, viz., chloracet-*p*-phenetide, $C_2H_5O.C_6H_4.NH.COCH_2Cl$, obtained by the action of chloride of chloracetyl on *p*-phenetidine in solution in toluene; this compound occurs in prisms or in leaflets fusible at 145—146°.

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THE CHEMICAL NEWS.

Vol. LXXX., No. 2071.

PHOTOGRAPHIC RESEARCHES ON PHOSPHORESCENT SPECTRA:

On Victorium, a New Element Associated with Yttrium.*

By Sir WILLIAM CROOKES, F.R.S.

It has long been known that certain substances enclosed in a vacuous glass bulb phosphoresce brightly when submitted to molecular bombardment from the negative pole of an induction coil. The ruby, emerald, diamond, alumina, yttria, samaria, and a large class of earthy oxides and sulphides, emit light under these circumstances. Examined in a spectroscope the light from some of these bodies gives an almost continuous spectrum, while that from others, such as alumina, yttria, and samaria, gives spectra of more or less sharp bands and lines. Since 1879 I have been working on these phosphorescent spectra, chiefly in connection with the earths of the yttria group, and by chemical fractionation I have succeeded in separating from this group bodies whose phosphorescent spectra consist chiefly of single groups of lines, other groups being absent. For the last six years the research has been extended beyond the visible spectrum, and photographs of the ultra-violet portion of the spectra are now being taken with a spectrograph with a complete quartz train. Some of the results of this investigation were exhibited at the Soirée of the Royal Society on the 3rd of May. A preliminary mention of the discovery of a new element was made in my Address to the British Association in September last, when I provisionally called it Monium; but for several reasons I now consider the name Victorium more appropriate.

The complicated scheme of fractionation carried on for so many years is illustrated in the accompanying diagram. This must be considered only as an indication of the methods employed, and not as an actual representation of every operation through which the material has passed. Crude yttria, from samarskite, gadolinite, cerite, and other similar minerals, is the raw material. The first operation is to free it roughly from earths of the cerium group—an operation effected by taking advantage of the fact that the double sulphates of potassium and the yttrium metals are easily soluble in saturated potassium sulphate solution, while the corresponding double sulphates of the cerium group of metals are difficultly soluble.

After this preliminary treatment, the crude yttria is converted into nitrate, represented by the topmost circle on the diagram. The nitrate is exposed to heat until it fuses to a clear liquid, care being taken to distribute the heat uniformly through the mass. Presently the liquid mass commences to decompose, giving off red vapours. After this has proceeded for a little time, the fused mass is carefully poured into water, and the liquid well boiled. A white precipitate of basic nitrate forms, while the undecomposed nitrates remain in solution. These are separated by filtration—the precipitate going to the right and the solution to the left. The basic nitrate is dissolved in nitric acid, and the right and left solutions are then evaporated to dryness and fused as before. Partial decomposition by heat again divides each of these portions into two lots, soluble and insoluble. The soluble from the left-hand lot goes still further to the left, and its insoluble portion to the right. The soluble from the right-hand portion goes to the left, where it mixes with the insoluble from the other portion, while its insoluble goes still further to the right. This series of operations is continued for as long a time as the material will hold out.* From a description the process seems to be more complicated than it really is, but a study of the diagram and the direction of the arrows make it clear. The number of times this operation is performed varies with each lot of earth fractionated. The portions submitted to fusion rapidly diminish in quantity, and the operation is continued until the material becomes too scanty.

The last horizontal line of fractions, spectroscopically examined in a radiant matter tube, shows differences in the visible spectrum. For many years I recorded these differences in coloured drawings, which have served on several occasions to illustrate papers before this Society.† In the year 1893 I commenced to record the differences between the various spectra by photographing them in a spectrograph having a complete quartz train, and since that time attention has chiefly been directed to the variations in the number, character, and positions of the lines and bands in the ultra-violet spectrum; these are more striking than those which are visible, and as they are self-recording results are more rapidly attained. A description of this instrument is given further on.

On placing the photographed spectra of one of the horizontal lines of earths in order, several differences are detected. One striking difference is seen in the behaviour of a group of lines in the ultra-violet. It is nearly absent in the end fractions, gradually becoming stronger towards the middle, and attaining a maximum in the fractions situate about two-thirds towards the right. This shows that at least three different bodies are present: one, the great bulk, having a nitrate difficult to decompose; another whose nitrate is easiest to decompose; and a third body, occupying an intermediate position, whose nitrate decomposition occurs at temperatures between that required by the others, but nearer that of the nitrate easiest decomposed.

The above method of fractionation is not so effectual if more than two bodies are present. In that case the process fails, in any reasonable time, to yield practically pure specimens of more than two out of a group of closely allied earths. Thus, if there are three earths—say, A, B, and C—whose positions in reference to the chemical process employed are in the written order of sequence, we may get a specimen of A as nearly as we please free from B and C, and a specimen of C as nearly as we please free from A and B, but we cannot get a specimen of B practically free from A and C. The law seems to be that to obtain practically pure specimens of three closely allied earths, it is essential to have recourse to at least two different chemical processes. The mere continued repetition of the same process will not do, unless indeed the operations are repeated such a vast number of times as to make the approximate expressions no longer applicable, even though the substances are chemically very close.

For this and other reasons it is advisable to change the method of fractionation after one process has been in operation for some time. It is evident that any process of fusion, crystallisation, or precipitation can only divide the mass of material into two parts, a soluble and insoluble portion, crystals and mother liquor; and after a time a balance of affinities seems to be established, and further fractionation appears to do little good. It is better then to change the operation.

Following the diagrammatic scheme, the portions of earths containing most victorium are collected together and fractionated by the crystallisation of the oxalates from a solution strongly acidulated with nitric acid in the following manner:—

To a boiling acid solution of the nitrate a small quantity

* A Paper read before the Royal Society, May 4, 1899.

* "On the Methods of Chemical Fractionation," British Association, Birmingham Meeting, 1886; Chemical News, vol. liv., p. 131.

† "On some New Elements in Gadolinite and Samarskite Detected Spectroscopically" (*Roy. Soc. Proc.*, No. 245, 1886, vol. xl., p. 502).

of hot solution of oxalic acid is added. The solution remains clear, and it is only after vigorous stirring that a small quantity of insoluble oxalate is formed. The whole is thrown on a hot-water filter and slightly washed with boiling water. To the boiling filtrate a fresh lot of hot solution of oxalic acid is added, and stirred till more insoluble oxalate comes down. This is again filtered off, and the operations of precipitating, stirring, filtering, and washing are repeated, always keeping the temperature as near the boiling-point as possible, until the whole of the earths are precipitated. Generally the initial earth is divided by this method of fractionation into from six to twelve portions. Each of these oxalates is dried, ignited, dissolved in nitric acid, and the above-described operations repeated. Photo-spectroscopic tests are constantly taken during the progress of this fractionation, and portions are mixed together according to the data thus obtained, as shown on the diagram by the lines joining the fractions. The object being to avoid lateral spreading as much as possible, and, while concentrating the special line-giving earth, to prevent its too great diffusion over a large number of fractions. When the fractionation by the oxalate method has proceeded for a considerable time, the fractions rich in victorium are collected together and submitted to another mode of treatment.

These fractions are converted into nitrates, and a small quantity is thrown out by partial decomposition by heat, according to the method already described. The filtrate is evaporated to dryness and again fused, so as to throw out a little more. This operation is repeated as long as any soluble nitrate is left. Generally from six to twelve portions are thus obtained. These form a regular series, differing according to the stability of the nitrate under heat. On testing, the victorium is found to concentrate in the centre portions, being less easily decomposed than the earths of the cerium group, and more easily decomposed than those of the yttrium group.

The fractions rich in victorium are converted into sulphates and mixed with a hot saturated solution of potassium sulphate. The precipitate is dissolved in boiling water and mixed with a further quantity of solution of potassium sulphate. This produces a small quantity of a precipitate. The filtrate from the first precipitate is also mixed with fresh potassium sulphate, and the operations are repeated, mixing the centre solutions to one lot and the side solutions to another, as shown by the lines on the diagram. It is found on photo-spectroscopic examination that the earths thrown out on each side are poorest in victorium, whilst those in the middle are richest. After a time no further concentration is effected in this manner, all the earths that can be removed as being more or less soluble in potassium sulphate having been eliminated.

In thus describing the method of fractionation, my object has been not so much to give a description of the plan actually carried out in the laboratory—for the details have varied with each operation—but to give an intelligible idea of the general manner in which a very complicated operation is effected. In the diagram I am supposing that one particular substance, victorium, is to be separated, and I have endeavoured to show its migrations and gradual concentration as the work progresses, by tinting the fractions where it mostly would concentrate; the depth of tint representing the amount of concentration.

In the purest condition yet obtained victoria is an earth of a pale brown colour, easily soluble in acids. It is less basic than yttria and more basic than most of the earths of the terbia group. In chemical characters it differs in many respects from yttria. From a hot nitric acid solution victorium oxalate precipitates before yttrium oxalate and after terbium oxalate. On fractional precipitation with potassium sulphate the double sulphate of victorium and potassium is seen to be less soluble than the corresponding yttrium salt, and more soluble than the double sulphates of potassium and the terbium and cerium groups. Victorium nitrate is a little more easily decomposed by heat than yttrium nitrate, but the difference is not sufficient to make this reaction a good means of separating victorium and yttrium. Fusing the nitrates can, however, be employed advantageously to separate mixed victoria and yttria from the bulk of their associated earths.

On the assumption that the oxide has the composition Vc_2O_3, the atomic weight of victorium is apparently not far from 117.

The photographed phosphorescent spectrum of victoria consists of a pair of strong lines at about λ 3120 and 3117; other fainter lines are at 3219, 3064, and 3060. Frequently the pair at 3120 and 3117 merge into one, but occasionally I have seen them quite distinct. The presence or absence of other earths has much influence on the sharpness of lines in phosphorescent spectra, and it is probable that these lines will be sharp and distinct when victoria is obtained quite free from its associates.

The best material for phosphorescing in the radiant matter tube is not the earth itself, but the anhydrous sulphate formed by heating the earth with strong sulphuric acid and driving off the excess of acid at a red heat. The sulphate thus produced, probably also containing some basic sulphate, is powdered and introduced into a bulb tube furnished with a quartz window, and a pair of thick aluminium poles sealed into the glass with stout platinum wires. The tube is well exhausted, keeping the current from a good induction coil going all the time. The pumping and sparking must continue until the earth glows with a pure light free from haze or cloudiness, and continues so to glow during the passage of the current without deterioration. The exposure in the spectrograph usually occupies an hour.

I give a diagrammatic plan of the two-prism spectrograph used in this research. It is furnished with two quartz prisms, quartz lenses, and condensers. The slit jaws are of quartz, cut and polished according to the method I described in the Chemical News, vol. lxxi., p. 175, April 11, 1895.

The prisms are made in two halves according to Cornu's plan; one half of each being right-handed and the other half left-handed. One of the lenses also is right-handed and the other left-handed. By this device the effect of double refraction is so completely neutralised that with a five-prism instrument it is impossible, under high magnifying power, to detect any duplication of the lines.

The lenses are each of 52 m.m. diameter and 350 m.m. focus. The focus of the least refrangible rays is longer than that of the most refrangible rays, and the sensitive film must therefore be set at an angle to get the extreme rays into focus at the same time. But this alone is not sufficient. The focal plane is not a flat surface, but is curved, and the film must therefore be curved,* and it is only when both these conditions are fulfilled that perfectly sharp images of spectral lines extending from the red to the high zinc line 2138·30 can be photographed on the same surface. Celluloid films are used, glass not being sufficiently flexible.

Using the middle position showing the whole spectrum on a plate, the angle is 40°, and the curvature is 190 m.m. radius.

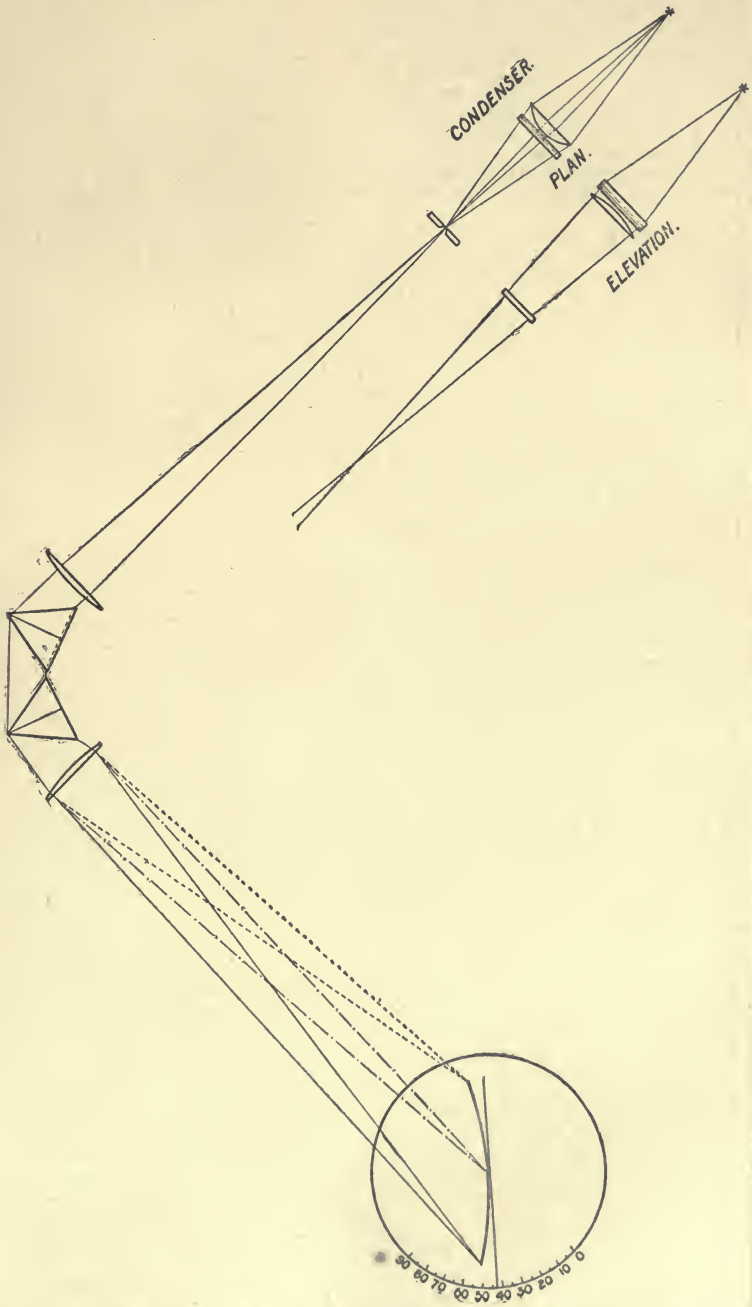
The condensers are of quartz, and are plano-cylindrical —one being double the focus of the other. The object of this, when spark-spectra are being photographed, is to concentrate on the slit a line instead of a point of light, as would be the case if ordinary lenses were used.

When photographing phosphorescent spectra—or, in fact, any spectra the wave-lengths of which are either unknown or require verification—I always photograph on the same film a standard spectrum, usually of an alloy of equal molecular weights of zinc, cadmium, tin, and mercury. This forms a hard, somewhat malleable alloy, giving throughout the whole photographic region lines

* Chemical News, vol. lxxii., p. 87, August 23, 1895; and vol. lxxiv., p. 259, November 27, 1896.

the wave-lengths of which are well known. The chief objection to this alloy is its volatility—the poles requiring frequent adjustment. Recently I have used pure iron for this purpose; this has the advantages of giving a great number of fine lines whose wave-lengths are accurately known, and not being very volatile, the poles do not rapidly wear away. If the poles are kept about 1 m.m. apart there is little or no interference from air lines.

The most simple method of applying the standard lines to an unknown spectrum is by the successive employment of two slightly overlapping diaphragms immediately behind the slit, one being used for the experimental and the other for the standard spectrum. In this way, without disturbing the instrument, the two spectra can be recorded on the plate one over the other; the overlap of 1 m.m. being in the optical centre of the train. The resulting negative is then transferred to a micrometer measuring machine of special construction, having a screw of $\frac{1}{100}$ of an inch pitch, and a means of accurately determining $\frac{1}{1000}$ of its revolution—thus measuring directly to the hundred-thousandth of an inch. In this way, in a five-prism spectrograph having lenses 700 m.m. focus, it is possible to determine wave-lengths of photographed lines to the sixth figure.



THE VOLUMETRIC ESTIMATION OF CARBON.

The moist combustion process has made analysts familiar with the equation—

$$3C+4CrO_3+6H_2SO_4=3CO_2+2Cr_2(SO_4)_3+6H_2O,$$

which represents the oxidation of carbon by chromic acid. Imbert and Compan's process (Chem. News, lxxix., 267), based on this reaction consists in measuring the excess of chromic acid added. This latter detail distinguishes it from similar processes in which the evolved CO_2 is generally either measured or absorbed and weighed.

Although the estimation of carbon depending on the measuring of the residual chromic acid strikes one as being something new, it can only be regarded as such in its application to elemental carbon as distinguished from carbon compounds. Certainly a significant and suggestive fact.

Cross and Bevan (*Journ. Chem. Soc.*, 1888, liii., 889), have investigated the combustion of cellulose compounds from the point of view of the oxidising substance by estimating the excess of chromic acid; and Phelps (Chem. News, lxxvi., 246), estimates carbon and oxygen simultaneously in a number of organic compounds by absorbing the evolved carbon dioxide and titrating the residual CrO_3.

Cross and Bevan found that the gas evolved on heating a carbon compound along with chromic and sulphuric acids consists of CO and CO_2, though in the more favourable tests the amount of the former was only some 2 or 3 per cent; they therefore measured the evolved gases in a graduated tube, a process altogether indifferent to the ratio $\frac{CO}{CO_2}$. Phelps, acting on Ludwig's observation that contact of carbon monoxide with a mixture of chromic and sulphuric acids, especially when hot, results in the oxidation of that gas to carbon dioxide, contrived to retain the products of the oxidation in prolonged contact with the oxidising mixture, and obtained very satisfactory results by estimating the CO_2 gravimetrically.

The advantage of measuring the residual CrO_3 compared with any form of measuring the CO_2 is obvious; the operation is easier, and involves no expensive or delicate contrivances. It is, however, equally obvious that although only carbon compounds can produce carbon dioxide, quite a number of bodies other than carbon can effect the reduction of chromic acid, and the need to separate those bodies must frequently counterbalance what advantage the method has over those usually adopted. This limits the method to a certain class of carbon compounds.

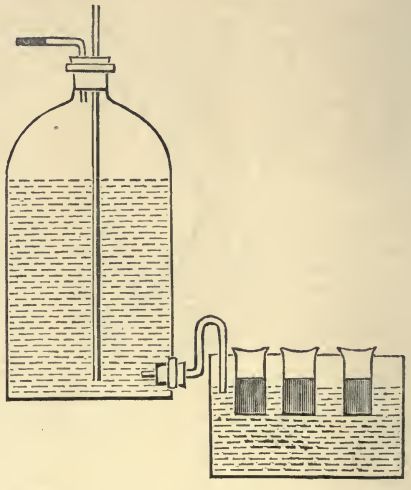
The application of the method to the estimation of carbon in steel illustrates its value, and indicates its limitations.

The carbon must be separated by treatment with any of the usual copper solutions, filtered off, and washed with a hot solution of dilute sulphuric acid until the washings no longer discharge a faint permanganate colouration. This is done to ensure the absence of ferrous and cuprous salts, and is very nearly successful. An examination of the carbonaceous residue and filter shows that the last traces of these salts are very difficult to remove. Besides carbon, hydrogen, and oxygen the residue contains (I refer only to ordinary steels), very small amounts of silica, sulphur, and phosphorus. The whole of these impurities, including the residual metallic salts, are of moment only in exceptional cases.

Instead of the seemingly roundabout means of estimating the excess of chromic acid adopted by Imbert and Compan most people would prefer to use ferrous sulphate or some other reducing agent which can be directly titrated by the bichromate used for the oxidation of the carbon. A solution of ferrous salt is so commonly used for other purposes where steel analysis is engaged in that in this connection it is as suitable a reagent as could be chosen.

A filter of asbestos, sand, or other non-oxidisable body must be used to separate the carbon, and it is necessary that during the final heating in the water-bath there should be more liquid than can be absorbed by the filtering medium. There must be enough, in fact, to permit free movement and ready admixture of the filter and oxidising solution, else the reaction, which is mainly active at this stage, is very much hindered. This difficulty is best avoided by making up a standard bichromate solution containing as much sulphuric acid as possible, short of precipitating the chromic acid. This will be about 500 or 600 c.c. per litre. Such a mixture may be heated in the water-bath without fear of decomposition; moreover, it is already so concentrated that a preliminary evaporation on the sand-bath, with its attendant dangers, is unnecessary. The carbon begins to be oxidised soon after placing in the bath, and it is completed for high percentage carbon steels in one or two hours. A sample digested for one hour* gave 1·15 per cent carbon; digested for two hours 1·18 per cent, and by combustion in oxygen and absorption of CO_2 1·18 per cent.

A convenient strength of bichromate solution is $\frac{4}{10}$ N. 25 c.c. of this solution oxidises 1 per cent of carbon from 3 grms. of steel. It is well known to be practicable even with N/10 bichromate solutions to titrate to 0·1 c.c., which under the above conditions is equivalent to only 0·001 per cent carbon, so that the errors of manipulation are of that insignificant kind which are so desirable in technical analysis.



For the analysis of pure carbon steels and pig-irons this process is worth serious consideration. It combines both speed and accuracy, and it is admirably suited for making estimations in batches, as is the daily practice in some works. The fact that the apparatus used is of the every-day order should commend it to the notice of those who have to do only an occasional sample as well as to instructors in laboratories where steel analysis is a subordinate subject.

During the oxidation of the carbon the asbestos entangles the CO_2, and is floated to the surface of the liquid; this requires the solution to be stirred a few times, but it retains the gas for some time in contact with the oxidising mixture, and thus favours the complete oxidation of any escaping carbon monoxide. When the asbestos lies quietly *in* the solution, and a gentle stir causes no bubbles to appear, the reaction is complete. The figure shows a convenient water-bath, and constant level arrangement.

* This time can be shortened more than one-half by nearly constant stirring.

Some test analyses are :—

	Percentage carbon.	
	Dry combustion.	Vol. process.
Ordinary steels	1·18	1·18
,, ,, ...	0·94	0·95
,, ,, ...	0·75	0·76
,, ,, ...	0·52	0·52
,, ,, ...	0·43	0·42
,, ,, ...	0·29	0·29
Ferro-nickels, 26 per cent Ni	0·29	0·28
,, ,, ,, ..	0·44	0·45
Pig-irons	4·02	4·03
,, ...	4·27	4·17
,, ...	4·15	4·08
,, ...	3·71	3·80

With the exception of the pig-irons the results of the volumetric estimations are all that could be desired, and if we take account of the fact the carbon of the pigs was chiefly graphitic, and that the samples were weighed from a packet of drillings, the differences are not greater than might obtain were dry combustions duplicated, and may well be accredited to the difficulty of taking a perfect sample.

The graphitic carbon from the pig-irons was only slowly oxidised by the chromic and sulphuric acids at the temperature of a water-bath. It was found, however, that the $\frac{1}{10}$ N bichromate made up as described could be heated for several hours in a calcium chloride bath at 130° C. without appreciable decomposition; that in fact it could be heated up to (not kept at) its boiling point, 155° C., without decomposition, although, as Cross and Bevan show, a mixture of chromic acid and *strong* sulphuric acid is slowly decomposed by prolonged exposure at a much lower temperature (105° C.). Now, at 130° C. the graphitic carbon of the pig-irons is completely oxidised in about an hour and a half, and the carbon liberated from ordinary steel in about twenty minutes.

Carbon in Special Steels.

It is no longer possible to assume that carbon, silicon, manganese, sulphur, and phosphorus are the only elements worth noticing in the analysis of a piece of steel. Modern warfare and the requirements of the engineer have led to the introduction of chromium, nickel, aluminum, copper, and tungsten, while the experimental enquiries of the steel-maker are responsible for the occasional presence of several other elements. All these things make a complete analysis of a sample of steel no mean problem, as the process available for one sample may be hopelessly misleading when applied to another. A need, supplied by no text-book, and demanded by the painful experience of most analysts, is some concise statement of the influence exerted on common processes by elements which, though not common, are yet not so rare as to be considered curiosities.

Where the special element in a steel passes into solution when treated with the solution of copper salt the volumetric process for estimating carbon is available and trustworthy. Those elements which remain with the carbonaceous residue are apt to introduce error and may invalidate the process altogether.

Tungsten Steels.—Nearly if not all the tungsten is to be found in the washed carbonaceous residue. In titrating, the excess of ferrous sulphate once oxidised continually reappears. This appears to be due to the fact that the metallic tungsten is only very slowly attacked in the concentrated mixture of sulphuric and chromic acids used for the digestion, but is much more readily attacked when the solution is diluted for titration.

I find that although the results, using the $\frac{1}{10}$ N bichromate solution, are approximately correct after an hour's digestion, they become slowly higher and higher if the digestion is continued. To meet this difficulty the bichromate was powdered, weighed out, and mixed with the carbonaceous residue suspended in concentrated sulphuric acid. Such a mixture of chromic and sulphuric acids has hardly any action on the tungsten, but, unfortunately, it does not by any means so readily oxidise the carbon liberated from combination with the iron. This point is again referred to below.

If a definite answer must be given to the enquiry, whether or not the volumetric process is available for tungsten steels, it can be said that it is, but in a somewhat limited and empirical degree. If no graphitic carbon is present, and the digestion be continued only until the asbestos sinks into the solution, and few or no bubbles appear on gentle stirring, the results will be only a few hundredths per cent out. If the digestion be made over several hours in a concentrated sulphuric solution the results are accurate, or only slightly high. In either case the digested solution should be rapidly passed through an abestos filter, so as to keep the tungsten out of the solution titrated. Or again, after oxidising the carbon the solution may be diluted several times with water, and left to complete the oxidation of the tungsten by gentle boiling; the amount of tungsten being otherwise determined, it may be allowed for on the assumption that $2CrO_3+W=Cr_2O_3+WO_3$ expresses the reaction; that is, one atom of carbon reduces as much chromic acid as 10·22 atoms of tungsten. Some very good results have been obtained in this way, but the process is a slow one, and is obviously of no value technically.

From the numerous experiments summarised in the two preceding paragraphs, it appeared that concentrated sulphuric acid along with chromic acid was a less effective oxidiser of combined carbon than a more dilute solution, and that the reverse was true of graphitic carbon. Acting on the principle that an impression, however strong, is less satisfying than a demonstrated fact, the following experiments were made :—

The carbon from 3 grms. of a 1·18 per cent carbon steel was digested with equal amounts of potassium bichromate in equal volumes of—(A) strong sulphuric acid. and (B) dilute, half and half, sulphuric acid. Also, the residue from 1½ grms. of pig-iron (total carbon 4·15, graphite 3·41 per cent) was similarly digested. The presence of combined carbon in the pig-iron favours the weaker solution, the results were—

	A. Per cent.	B. Per cent.
Combined Carbon.		
Digested one hour..	0·65	1·19
Digested two hours	0·73	1·19
Graphitic Carbon.		
Digested one hour..	3·58	2·57
Digested two hours	3·70	3·11

These results have considerable interest in connection with the oxidation of carbon with chromic and sulphuric acid in the ordinary moist combustion process. In text-book descriptions the aim appears to be to have the sulphuric acid in as concentrated a form as possible, and to heat the mixture until fumes of sulphuric anhydride are evolved. The fumes are a source of danger, in that they pass the purifying train and are, partially at least, absorbed in the potash bulbs. It is hardly possible to resist the conclusion that the carbon would be as readily—or generally, more readily—oxidised by a chromic acid solution containing only about 50 per cent sulphuric acid, which could be raised to boiling without any appreciable evolution of sulphuric anhydride. The only fear to be entertained is that the $\frac{CO}{CO_2}$ ratio might be increased; this, however, is matter for experiment rather than speculation. Observations covering this point, and the most effective percentage of sulphuric acid to use for this particular purpose, are being made.

Molybdenum Steels.—Molybdenum does not interfere, although it partially accompanies the carbon. In neither

of the samples examined containing (A) 3 and (B) 8 per cent of molybdenum respectively was there any indication of a reducing action after the diluted solution had been titrated, as is the case with tungsten steels.

	C per cent grav.	C per cent vol.
A	0·98	0·99 and 0·98
B	3·73	3·72
C*	1·28	1·26

* Contains 3 per cent each of Mo and W.

Chrome Steels. — Chromium is said to exist in the carbonaceous residue as a double carbide of chromium and iron. Both these metals exert a reducing action on the chromic acid, so that anything but traces of chromium completely invalidates the method. The process may, however, be of service in determining the constitution of the carbonaceous residues from chrome steels.

J. T.

THE PHYSIOLOGICAL EFFECT OF CREATIN AND CREATININ, AND THEIR VALUE AS NUTRIENTS.*

By J. W. MALLET, M.D., LL.D.,
Professor of Chemistry in the University of Virginia.

(Continued from p. 45).

Materials Employed in the Present Investigation.

A GOOD deal was hoped from the use in experiment of larger quantities of the flesh bases in a state of purity than had previously been used, so that from the methods (necessarily not rigorously exact) of determining these substances as eliminated in the urine, results of a fairly decisive character might be obtained. The writer was fortunate enough (thanks to the kindness of a friend and former pupil, now connected with a firm preparing a well-known meat extract) to possess several hundred grms. each of almost chemically pure creatin and creatinin. These were very carefully purified further and re-crystallised, and furnished abundant material for the physiological experiments undertaken. They were quite free from mineral impurity of any kind. Each was tested for the presence of the other, and, by the fractional use of solvents, each was ascertained to be quite uniform in character.

The general properties of the creatin and creatinin so prepared were found to agree in general with the description given in the text-books, but a few special points of detail may be noted.

According to Liebig's description creatin "has a somewhat bitter taste, and scratches in the throat," while "creatinin in the state of concentrated solution has a caustic taste like that of dilute ammonia." Both of these substances as prepared by the author, when taken into the mouth in large quantity and swallowed with a little pure water, had a bitter taste, not very strong or disagreeable. This taste was comparatively slight in the case of creatin, and much more marked in that of creatinin, as might be expected from their different degrees of solubility.

The statements of Liebig and G. S. Johnson do not agree in regard to the solubility of creatinin in alcohol, the former finding it three times as soluble as did the latter. My determinations gave the following results:—100 grms. of 90 per cent ethyl alcohol dissolved 0·018 grm. of creatin or 0·454 grm. of creatinin at 19·2° C. Under these conditions, therefore, creatinin is more than twenty-five times as soluble as creatin. For the analytical separations to be made it was important to know also the solubility of urea in alcohol of the strength employed. On the authority of Prout it is stated that one part of urea dissolves in five parts of alcohol of specific gravity 0·816 in the cold. I found that 100 grms. of 90 per cent alcohol dissolved 11·526 grms. of pure urea at 19·2° C., so that under these conditions it is more than twenty-four times as soluble as creatinin.

Some discrepancy has also been observed in the recorded statements as to the reactions of these flesh bases with litmus paper. According to the original observation of Chevreul, uncontradicted by later experimenters, creatin is neutral to vegetable colours, while Liebig and others have reported creatinin as distinctly alkaline, changing red litmus to blue and reddening turmeric. However, Salkowksi found that a strongly alkaline sample left an alkaline ash on ignition, and that pure creatinin was quite free from alkaline reaction. The creatin used by me was quite neutral to litmus paper; the creatinin, although free from ash, gave an extremely faint, scarcely perceptible, alkaline reaction.

In view of the readiness with which creatin may be converted into creatinin, and *vice versâ*, and in view also of the fact that for the purposes of this investigation they would have to be sought for and determined in the presence of the urea of urine, the behaviour of creatin, creatinin, and urea with reagents had to be examined. In this direction, also, results were obtained not altogether in accord with the statements of some of the text-books in general use. Thus, Allen (A. H. Allen; "Commercial Organic Analysis," vol. iii., Pt. III., p. 287), says: "Creatin is also distinguished from creatinin by being unprecipitated by a solution of phosphotungstic acid in presence of hydrochloric acid."

Using fairly strong aqueous solutions of the flesh bases, I found that the hydrochloric acid solution of phosphotungstic acid gave with creatin a small crystalline precipitate, forming gradually; with creatinin also a precipitate, but more copious, and forming more promptly.

In O. Hammarsten's "Text-book of Physiological Chemistry" (Authorised Translation, by J. A. Mandel, p. 348), the statement is made in reference to creatinin that "it is precipitated like urea, with mercuric-nitrate solution." I found that even the most concentrated aqueous solution of creatin or creatinin gave no precipitate with a solution of mercuric nitrate containing just enough free nitric acid to make it clear, while the reagent gave an abundant precipitate with a solution of urea. If to the mixture of creatin or creatinin solution with the acid mercuric nitrate a dilute alkali was added, a white precipitate was readily formed.

It may also be mentioned that the specially valuable precipitant for creatinin, zinc chloride,* also gives precipitates—flocculent rather than crystalline—with both creatin and urea. These precipitates are moderate in amount, but gradually increase, so that separation from these substances must be effected before the precipitation of creatinin-zinc chloride can be made the basis for an accurate determination.

It seemed desirable to secure new determinations of the heat of combustion of creatin and creatinin, using a portion of the material prepared for these experiments. Such determinations were made, by the kindly offered aid of Prof. W. O. Atwater, in the chemical laboratory of the Storrs Connecticut Experiment Station, at Middletown, Conn., with the improved form of bomb-calorimeter. The specimens of air-dried creatin and creatinin were dried in air for five hours at 96°, and gave, for water-free substance, creatin 88·08 per cent and 88·075 per cent, and creatinin 93·66 per cent and 93·70 per cent.

These dried samples were burned, and yielded results as below. They kindled with great difficulty, not even naphthalene serving to ignite them. The substance was finally burned by inclosing in a gelatin capsule of known weight and making allowance for the heat of combustion

* *Bulletin*, No. 66, United States Department of Agriculture, Office of Experiment Stations.

* The investigations of the author confirm the statement of Schäfer ("Physiology," p. 100), that unless the proper conditions be exactly observed the precipitation of creatinin with zinc chloride is very uncertain and unsatisfactory.

of the capsule. The heats of combustion of 1 grm. of water-free substance were, in large calories,—

	Calories.
Creatin, first combustion	4·269
Creatin, second combustion ..	4·264
Average..	4·267
Creatinin, first combustion ..	4·578
Creatinin, second combustion ..	4·588
Average..	4·583

From these results we have, as the value for the molecular heat of combustion: — Creatin, 559 calories; creatinin, 517·9 calories; and the conversion in the human body of each molecule counted in grms.) of creatin into creatinin involves heat *consumption* to the extent of 41·1 calories.

Method Devised and Employed for Separation of Creatin, Creatinin, and Urea in Urine.

Before stating the method worked out and adopted for the quantitative determination of the three substances, creatin, creatinin, and urea, in urine containing the usual normal constituents, it may be well to note the character and strength of the reagent solutions used. It was desirable to have these in a fairly concentrated form, so as to reduce as much as possible the volume of liquid to be evaporated, and thus diminish the chance of creatin becoming converted into creatinin, or the reverse.

The reagents were as follows;—

1. Milk of lime, a thin fluid pulp of pure calcium hydroxide, for the most part in suspension, in water.

2. Aqueous solution of pure neutral calcium nitrate (200 grms. to the litre). The object of using nitrate rather than chloride for the removal of phosphates, &c., was to avoid the addition of large quantities of mercuric nitrate, which would otherwise have been necessary before urea could be precipitated. A calcium rather than a barium salt was used, notwithstanding the consequent failure properly to remove sulphates. The calcium nitrate, added as such, as well as that subsequently formed in the liquid under treatment, is easily soluble in alcohol, while barium nitrate is not.

3. Dilute nitric acid; 100 grms. acid per litre of water.

4. Aqueous solution of mercuric nitrate; 300 grms. to the litre, with just enough free nitric acid to render the solution clear and prevent formation of a basic salt.

5. Alcoholic solution of zinc chloride; a nearly saturated solution in 90 per cent alcohol.

6. Alcoholic solution of sodium acetate; a saturated solution in 90 per cent alcohol.

7. Acetic acid; about 40 per cent.

8. Sodium hypobromite, prepared by mixing equal volumes of an aqueous solution of sodium hydroxide (340 grms. to the litre) and one of bromine (200 grms.) and potassium bromide (240 grms.) per litre.

To the portion of urine to be treated—usually about 250 or 300 c.c.—there was added, with constant stirring, milk of lime until the reaction was distinctly alkaline and 20 c.c. of the solution of calcium nitrate. After standing for an hour the turbid liquid was filtered, drained with the aid of a filter-pump, and washed once or twice with a small amount of water. The filtrate was tested with a drop or two of the calcium nitrate solution in order to make sure that precipitation of phosphates, &c., was complete. It was then accurately neutralised with a few drops of dilute nitric acid, and urea was precipitated with the solution of mercuric nitrate, avoiding any large excess of the reagent. As soon as the flocculent precipitate had settled, and before it had time to become crystalline and granular, it was filtered off with a filter-pump and washed sparingly with water. The filtrate was tested to make sure that the precipitation of urea was complete.

This precipitate was washed off from the filter into a beaker (owing to its bulkiness more than one filter had sometimes to be used), well stirred up with water, and decomposed by a rapid stream of sulphuretted hydrogen gas. The gas was passed through the liquid long enough to insure complete conversion of all the mercury into sulphide. The mercuric sulphide was removed by filtering, the filtrate evaporated to dryness at a gentle heat over a water-bath, and the residual urea nitrate weighed, a check upon its amount being obtained by re-dissolving it, and from an aliquot part determining the nitrogen evolved by means of sodium hypobromite, adding pure potassium cyanate and introducing the bromine solution separately after the caustic soda, as recommended by Allen. This precipitation of urea by mercuric nitrate in acid solution is not complete, but it largely reduces the amount to be separated from the flesh bases. In some experiments urea was not determined, and in some of these the precipitation with mercuric nitrate was omitted. In view of the observation of Meissner that the solubility of creatin in alcohol is increased by the presence of urea, it is better to remove the bulk of the urea in every case.

Through the liquid filtered off from the precipitate produced by mercuric nitrate a stream of sulphuretted hydrogen was passed as long as it gave rise to any precipitate, and mercuric sulphide was removed by filtration. The filtrate was *very accurately* neutralised by milk of lime, and evaporated at a temperature not exceeding 40° C. in a partial vacuum produced by a good filter-pump. When the volume had been reduced to about 5 c.c. alcohol of 90 per cent was added in such quantity as would little more than suffice to hold in solution the quantity of creatinin supposed to be present. A little absolute alcohol was used to make, with the small quantity of water remaining unevaporated, a uniform strength for the whole of 90 per cent. The alcoholic liquid was allowed to stand for three or four hours, being occasionally stirred, and was then filtered.

The residue left upon the filter, having been lightly washed with 90 per cent alcohol, was treated with a small amount of boiling water and again filtered. The undissolved matter on the filter, consisting mainly of crystalline calcium sulphate, was washed twice with small quantities of boiling water. The aqueous filtrate was evaporated to dryness over a water-bath, and the residue, creatin, was dried at 100° C. and weighed. The creatin was not absolutely pure, still retaining a little calcium sulphate and some organic compound of calcium which left lime on being strongly ignited. The creatin was re-dissolved and re-crystallised, the microscopic appearance of the crystals was observed, and two or three tests for the identity of the substance applied (silver nitrate and potash, picric acid, &c.).

The alcoholic solution filtered off from the creatin, &c., was concentrated by evaporation to about one-fifth of its original volume; a little of the alcoholic solution of sodium acetate was added, with enough acetic acid to produce slightly acid reaction. The creatinin was then precipitated by the addition of alcoholic solution of zinc chloride, allowing the liquid to stand in a well-covered vessel for three or four days before filtering. The creatinin-zinc chloride was washed on a dried filter with a moderate amount of 90 per cent alcohol, dried at 100° C., and weighed. The whole volume of alcohol, including the washings, was noted and a correction applied for the small amount of creatinin-zinc chloride retained in it in solution. After weighing, the precipitate was carefully examined with a microscope to see that it was free from sodium chloride or other visible impurities, and in two or three instances its identity was still further established by determinations of zinc and chlorine.

Having ascertained that the precipitation of creatinin by zinc chloride was complete, a determination of such urea as remained in the filtrate was made with an aliquot part of it by means of sodium hypobromite, and the result added to that from the urea previously recovered as nitrate.

In carrying out this process there was found to be considerable advantage in using of each reagent—*e.g.*, mercuric nitrate and zinc chloride—an amount calculated on the basis of approximate knowledge of the quantities present of the substances to be determined, such as to provide for a very small surplus only of the reagent, always, however, testing afterwards to make sure that enough had been employed.

Before proceeding to the physiological work a number of experiments were made to ascertain how far the analytical method might be trusted. Known amounts of creatin, creatinin, and urea were added to a portion of normal urine. Comparative determinations of these three substances were then made. Similar determinations were also made in another sample of the same urine which had not received such additions. Neglecting three or four preliminary experiments, in which the method was being worked out and in which the procedure was not uniform, the results given below were obtained. In each case the urine employed was the mixed total excretion of twenty-four hours. Of this two samples were taken, each one-fifth of the whole. To facilitate comparison with other results recorded later, the figures actually obtained have been multiplied by five, so that the report stands as for the whole daily quantity.

In the following table is shown the amount of urea, creatinin, and creatin found in nine samples of the total normal urine excreted in twenty-four hours:—

Constituents of Normal Urine.

Number of sample.	Urea. Grms.	Creatinin. Grm.	Creatin. Grms.
1	29·246	0·781	—
2	29·092	0·832	—
3	28·608	0·894	—
4	30·125	0·695	—
5	28·538	0·753	—
6	28·866	0·844	—
7	27·764	0·869	—
8	28·933	0·815	—
9	29·122	0·872	—

In the following table is shown the amount of urea, creatinin, and creatin added to ten samples of the same urine mentioned above, together with the amount and percentage of added material recovered.

Materials Added to Urine and Amounts Recovered.

Number of sample.	Additions made to urine. Urea. Grms.	Creatinin. Grms.	Creatin. Grms.	Added materials recovered.* Urea. Grms.	Creatinin. Grms.	Creatin. Grms.	Urea. Per cent.	Creatinin. Per cent.	Creatin. Per cent.
1.	2	1	—	1·948	0·956	—	97·4	95·6	—
2.	2	1	—	1·941	0·948	—	97·0	94·8	—
3.	3	2	—	2·895	1·898	—	96·5	94·9	—
4.	5	3	1	4·846	2·856	0·863	96·9	95·2	86·3
5.	5	4	1	4·721	3·903	0·845	94·4	97·6	84·5
6.	7	5	1	6·811	4·776	0·856	97·3	95·5	85·6
7.	8	5	2	7·736	4·635	1·769	96·7	92·7	88·4
8.	8	8	2	7·592	7·609	1·774	94·9	95·1	88·7
9.	10	10	3	9·683	9·392	2·635	96·8	93·9	87·8
Average							96·4	95·0	86·9

* After deducting from the amounts actually found those due to the normal constituents.

Although the process used is less favourable to the accurate determination of creatin than to that of creatinin, it may well be suspected that the difference between the two is not quite so great as seems to be shown by these figures, it being quite conceivable that, in spite of the precautions taken, some little conversion of creatin into creatinin may have occurred under the treatment applied. This would of course tend to raise the results obtained for the latter substance and to lower those of the former.

(To be continued).

THE ESTIMATION OF OXYGEN IN COAL-GAS.

By Dr. H. LUBBERGER.

The estimation of the oxygen contained in coal-gas is not an easy operation, as it constitutes hardly 0·2 or 0·3 per cent of the total volume; that is to say, with the ordinary gasometric apparatus we have to measure 0·2 to 0·3 c.c. of gas. It is, however, important to have a method enabling us to estimate exactly the oxygen in ordinary coal-gas, considering that it is more and more recognised that a small addition of air to the raw gas helps the purification very considerably.

It is evident that as the apparatus of Bunte or of Hempel do not allow of a volumetric determination, we might perhaps make use of Rüdorf's apparatus. With a receiver of 1 litre capacity each per cent of oxygen would be represented by a diminution of volume of 1 c.c. But the readings would be false, inasmuch as other gases accompany coal-gas, as well as oxygen, and they would be absorbed in quantities too great to overlook.

The process lately described by Dr. Pfeiffer (*Journ. f. Gasbeleuchtung*, 1897, p. 356), for estimating the proportion of oxygen contained in coal-gas, necessitates the use of an empirical solution of caramel, which would certainly not remain unchanged for years, which is a serious inconvenience.

I have attempted to modify E. W. Winkler's process (*Berichte*, 1888, xxi., II., 2843), in such a manner as to make it applicable with Bunte's burette.

This process depends on the oxidation, by means of the oxygen dissolved in water, of an alkaline solution of manganous hydroxide to the state of manganic hydroxide. By adding potassic iodide and hydrochloric acid, a quantity of iodine is set free equal to the amount of oxygen dissolved, and it is only necessary to titrate with a solution of hyposulphite to estimate the quantity of oxygen present.

The following are the reagents necessary:—

1. A solution of potassic iodide; 10 grms. of caustic soda, 15 grms. of crystallised Seignette salts, and 8·5 grms. of potassic iodide are dissolved in 300 c.c. of water.

2. A manganous solution; 14·5 grms. of manganous sulphate ($MnSO_4+5H_2O$) in 100 c.c. of water.

3. A centinormal solution of hyposulphite of soda; 2·48 grms. of hyposulphite ($Na_2S_2O_3+5H_2O$) dissolved in 1 litre of water.

It is further necessary to have water free from air prepared by Pfeiffer's method (*Journ. f. Gasbeleuchtung und Wasserversorgung*, 1897, p. 356).

To introduce the gas to be analysed into the burette, the latter is filled with water, and the gas passed in through the upper tap. The lower tap is then closed, and the upper one turned through an angle of 180°.

During this operation the gas being in the burette

under pressure drives the air out from the passage through the tap. The tube through which the gas is passed is then removed, and the outer side of the tap is covered with a short piece of indiarubber tube plugged with a bit of glass rod. About 5 c.c. of water free from air are poured in through the funnel, and allowed to run into the burette in such quantity that it forms a layer of about 1 c.c. above the lower tap. The lower tap is then carefully opened, and enough water allowed to run out to fill the capillary tube which is above and below the tap.

This method of working applies to the case of a sample of gas taken from a pipe where it is under pressure, but when the gas has to be pumped from the pipe it is necessary to fill the taps with water at first to prevent any air entering the burette during the subsequent treatment. The burette thus filled is fixed on its support, and water free from air is passed in through the upper end, up to the third degree above zero, and the excess of gas is allowed to escape through the three-way tap, the funnel being full. After reading the level the water is run off down to the tap and the funnel emptied.

The further treatment of the gas varies according to whether the sample of gas was taken before or after passing through the purifiers; that is to say, according to whether it contained sulphuretted hydrogen or not.

I. *Gas taken after Purification—that is to say, Free from Sulphuretted Hydrogen.*—One c.c. of manganous solution is passed in by the upper tap, and then 30 c.c. of potassic iodide solution by the lower tap. The burette is then well shaken in such a manner that the liquid contained in it passes up and down the whole length of the burette at each shake. This operation is continued for ten minutes; after this, 1 c.c. of concentrated hydrochloric acid (at 25 per cent) is passed in through the lower end, and the whole turned over. In the case of a gas containing oxygen, iodine is set at liberty. The funnel is then filled with ordinary distilled water, and the contents of the burette are then transferred to a beaker. We then add a little 1 per cent starch, and titrate with centinormal hyposulphite of soda until the blue colour disappears. It is necessary to subtract 0·3 c.c. from the volume of hyposulphite used, and the proportion of oxygen present is then calculated, each 1 c.c. of hyposulphite being equivalent to 0·06 c.c. of oxygen; that is to say, 0·06 per cent by volume when we take 100 c.c. of gas. We can perform the whole operation in the same burette, but in this case the correction to be made would be 0·06 c.c.

II. *Gas taken before Purification—that is to say, containing Sulphuretted Hydrogen.*—As sulphuretted hydrogen interferes with the operation, and is not without action on the reagents employed, it should be previously removed. After running off the water 2 c.c. of iodine solution (5 grms. of iodine and 10 grms. of potassic iodide in 100 c.c. of water) are passed into the burette by the lower tap, and shaken vigorously several times.

The solution of iodine is run off, and the last traces removed by washing with the smallest possible quantity of water free from air, introduced by the upper tap. The last washings should be without action on starch. Continue the operation as in the first case.

Analysis gives the following results :—

Oxygen added. C.c.	Oxygen found. C.c.	Oxygen added. C.c.	Oxygen found. C.c.
0·104	0·099	0·313	0·297
0·104	0·111	0·418	0·427
0·209	0·204	0·418	0·409
0·209	0·186	0·627	0·657
0·209	0·210		

The small differences arise from the fact that we take 1·0 c.c. of hyposulphite as being equivalent to 0·06 c.c. of oxygen, without allowing for temperature and pressure. But as this is purely a commercial method such small differences may be neglected.—*Journ. f. Gasbeleucht. und Wasserversorg.*, xii., p. 695.

ON A TEST, BY THE FREEZING-POINT METHOD, OF THE IONISATION COEFFICIENTS DETERMINED BY THE CONDUCTIVITY METHOD, FOR SOLUTIONS CONTAINING POTASSIUM AND SODIUM SULPHATES.*

By E. H. ARCHIBALD, M.Sc.,
1851 Exhibition Science Scholar, Dalhousie College, Halifax, N.S.

(Continued from p. 47).

Determination of Equivalent Conductivity at Infinite Dilution for 0° C.

FOR this purpose a series of simple solutions of each electrolyte, of concentrations ranging from 0·01 to 0·0001 grm.-equivalents per litre, were prepared, and their conductivities were measured both at 18° C. and at 0° C. The conductivity of the water used in their preparation was also measured at both temperatures and subtracted in each case from the conductivity of the solutions. Table I. gives the results of the observations, together with the values of the temperature coefficients, $(\mu_{18}-\mu_0)/\mu_{18}$. Concentrations are expressed in grm.-equivalents of anhydrous salt per litre and conductivities in terms of 10^{-8} times the conductivity of mercury at 0° C. The conductivities at 18° were tested by comparison with Kohlrausch's values; these values, when plotted on co-ordinate paper, being found to lie practically on the same curve as mine.

It will be seen that the temperature coefficients for potassium sulphate solutions diminish with increase of dilution while those for sodium sulphate increase. This result† was so unexpected that I thought it well to repeat the observations, the result being substantiated by the repetition.

It will be seen, also, that in both cases the coefficients reach constant values as concentration is diminished; in the case of $\frac{1}{2}K_2SO_4$ from a concentration of 0·0004 on, in that of $\frac{1}{2}Na_2SO_4$ from 0·0006 on. Assuming, then, that these values will hold for infinite dilution, the equivalent conductivities at infinite dilution for 0° C. may be determined from Kohlrausch's values (*Wied. Ann.*, 1893, l., 406) for 18° C., viz., 1270×10^{-8} and 1070×10^{-8} for $\frac{1}{2}K_2SO_4$ and $\frac{1}{2}Na_2SO_4$ respectively. They were found thus to have the values 800×10^{-8} and 646×10^{-8} respectively, expressed in terms of the conductivity of mercury at 0° C.

Determination of the Ionisation Coefficients of Simple Solutions.

Both for the purpose of finding how closely the lowering of the freezing-point could be calculated for simple solutions and for the purpose of determining the ionisation coefficients of the electrolytes in the mixtures, it was necessary to know the ionisation coefficients of a sufficiently extended series of simple solutions of the two electrolytes. Table II. contains the observations of conductivity made for this purpose, together with the values of the ionisation coefficients calculated on the assumption that for simple solutions they are equal to the ratios of the equivalent conductivity to the equivalent conductivity at infinite dilution. The table gives also the ionisation coefficients at 18° C. obtained from the conductivity observations of former papers (*Trans. N.S. Inst. Sci.*, 1897-8, ix., 291 and 307). These quantities are not needed for the present purpose. But the knowledge of the ionisation coefficients at 0° enables us to determine how, in the case of the electrolytes under consideration, the state of ionisation in

* From the *Transactions of the Nova Scotian Institute of Science*, vol. x., Session 1898-99.

† The results of this table are in close agreement with those obtained by Deguisne ("Dissertation," Strassburg, 1895), of which Mr. Archibald was not aware.—J. G. M.

Table I.

Potassium Sulphate Solutions.

Concentration at 18° C.	Equivalent conductivity (μ). At 18° C.	At 0° C.	$(\mu_{18}-\mu_0)/\mu_{18}$.
0·010	1099	687	0·375
0·008	1116	698	0·375
0·005	1142	716	0·373
0·004	1155	723	0·374
0·002	1180	740	0·373
0·001	1206	757	0·372
0·0008	1213	762	0·372
0·0006	1221	768	0·371
0·0005	1225	771	0·371
0·0004	1230	775	0·370
0·0002	1240	781	0·370
0·0001	1248	786	0·370

Sodium Sulphate Solutions.

Concentration at 18° C.	Equivalent conductivity (μ). At 18° C.	At 0° C.	$(\mu_{18}-\mu_0)/\mu_{18}$.
0·010	907	555	0·388
0·008	919	562	0·389
0·005	946	577	0·390
—	—	—	—
0·002	981	596	0·393
0·001	997	604	0·394
0·0008	1003	607	0·395
0·0006	1008	609	0·396
0·0005	1012	611	0·396
—	—	—	—
0·0002	1027	620	0·396
0·0001	1036	626	0·396

simple solutions varies with the temperature. Concentrations and conductivities are expressed in terms of the same units as in Table I.

Table II.

Concentration at 18° C.	Equivalent conductivity at 0° C. $\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.	Ionisation coefficients. K_2SO_4. At 18° C.	At 0° C.	Na_2SO_4. At 18° C.	At 0° C.
0·050	604·2	486·0	0·757	0·755	0·733	0·752
0·055	598·0	480·0	0·750	0·748	0·728	0·743
0·060	594·1	475·5	0·745	0·743	0·723	0·736
0·070	585·4	466·5	0·736	0·732	0·715	0·722
0·080	577·5	460·0	0·723	0·722	0·703	0·712
0·100	564·0	448·5	0·706	0·705	0·686	0·694
0·125	547·5	434·0	—	0·684	—	0·672
0·150	535·0	422·5	—	0·669	—	0·654
0·200	516·0	403·1	0·650	0·645	0·601	0·624
0·250	503·0	387·4	0·634	0·629	0·586	0·600
0·300	493·0	373·5	0·620	0·616	0·570	0·578
0·350	485·0	362·4	0·605	0·606	0·556	0·561
0·400	478·0	353·0	0·595	0·598	0·545	0·546
0·450	473·0	345·5	0·587	0·591	0·533	0·535
0·500	470·0	339·6	0·580	0·588	0·522	0·525
0·600	466·0	330·0	0·567	0·583	0·506	0·511
0·700	464·0	324·2	0·551	0·580	0·498	0·501

It appears from these results that in the case of solutions of potassium sulphate the ionisation coefficient increases very slightly with rise of temperature between 0° and 18° C. from a concentration of 0·05 to one of about 0·35, and that from this concentration to one of at least 0·7 it decreases, the magnitude of the decrement increasing rapidly with the concentration, and amounting at a concentration of 0·7 to 5 per cent. In the case of sodium sulphate, the coefficient diminishes with rise of temperature throughout the whole range of concentration observed, the amount of the decrement diminishing with increase of concentration, until at a concentration of 0·7 it is only 0·6 per cent.

Method of Measuring Depression of the Freezing-point.

Of the different methods described for the determination of the freezing-point of salt solutions, that of Loomis (*Phys. Review*, 1893, i., 199 and 274; 1896, iii., 270) appeared to me the best, and to give the most concordant results. His method was accordingly followed in making the measurements below.

As it is most essential that the temperature of the room where the observations are made should be near zero and as constant as possible, the measurements were carried out during the winter months in a basement room of Dalhousie College building, where it was found possible to keep the temperature below 2° C. and constant to within 0·5 of a degree for a couple of hours at a time. No measurements were made while the temperature of the room was above 2° C.

The thermometer was of the ordinary Beckman form, graduated to 0·01 of a degree. No reading microscope being available, I had to be satisfied with the use of an ordinary hand lens for this purpose. Nevertheless, as the divisions of the scale were about 0·6 m.m. in length, I am quite satisfied that I was able to read the temperatures to at least 0·001 degree. The following readings of the thermometer made in an experiment for determining the freezing-point of water would seem to imply that I succeeded in reading even more closely:—2·3415, 2·3410, 2·3420, 2·3415, 2·3420. Mean reading, 2·3416. Greatest divergence from mean, 0·0006.

The thermometer had never been calibrated, and as apparatus for this purpose was not available, I did not attempt to calibrate it myself. The length of scale used for the following measurements, however, was less than what corresponded to 1·4 degree, and for the more dilute solutions, say below 0·1 grm.-equivalent per litre, less than what corresponded to 0·2 of a degree.

The freezing and melting baths were each of earthenware, about 32 c.m. long and with an internal diameter of about 9 c.m. In the former was a mixture of snow and water with enough common salt added to keep the temperature at about −12° C. The latter contained a mixture of snow and water, the temperature of which was about 0·2° C.

The protection bath, which was of glass 35 c.m. deep and 8 c.m. in diameter, was provided with a covering of felt to minimise the effect of the surrounding air. It contained a mixture of snow and air with sufficient salt added to keep the temperature from 0·3° to 0·28° below the freezing-point of the solutions to be measured. After some experience had been gained, little trouble was found in keeping the temperature of this bath constant within a twentieth of a degree during several observations of any one solution.

The freezing tubes first tried were of the following dimensions:—The inner one 22 c.m. long with an external diameter of 2·4 c.m., the outer one 20 c.m. long with an internal diameter of 2·7 c.m., the thickness of the glass of both tubes being 1 m.m. There was thus an air space of about 1·5 m.m. between the tubes. This was found to be too great, as shown by its being difficult to prevent ice from forming around the bulb of the thermometer despite the most vigorous stirring. The next ones tried were as follows:—The inner tube was 28 c.m. long with an external diameter of 2·7 c.m., the outer tube 26 c.m. long with an internal diameter of 2·85 c.m., the thickness of the glass being the same as before. There was thus an air space of about 0·7 m.m. between the tubes. This was found to be hardly enough, as there was a tendency for the ice to form on the walls of the tube and thus cause much delay. As I worked with 75 c.c. of solution, the greater length of these tubes allowed the solution to be immersed well into the bath, rendering it almost free from the influence of the outside temperature. The inner tube was therefore retained and an outer tube provided of

about the same length and thickness of walls, but with an internal diameter of 2·88 c.m., thus leaving an air space of about 0·9 m.m. between the tubes. This gave complete satisfaction. With uniform stirring no tendency was observed for the ice to form on the walls of the tube or on the bulb of the thermometer, or to freeze in a mass. The inner tube had its lower end re-entrant, as recommended by Loomis.

I should like to draw attention to the importance of having the air space between the two tubes of the proper size. If the importance of this point has been noted by former observers it has escaped me.

The hammer used for tapping the thermometer was part of a small electric bell and was covered with a piece of thick rubber tubing. It was found to be very essential to drive the hammer so that the blows on the thermometer might be of uniform strength. Some difficulty was met with in attaining that end; but by careful attention to the strength of the current what appeared to be sufficient uniformity was attained.

The stirrer was of the ordinary ring form, the upright rod passing through a glass tube, the upper end of which was constricted, and the lower so far from the solution that the wetted portion of the stirrer could not touch it. A stop on the upright rod limited the extent of the stroke so that the ring would not leave the solution, and ensured the equality of the strokes. It was worked by hand as uniformly as possible.

The over-cooling was seldom over 0·1°, owing doubtless to the low temperature of the room in which the observations were made. There was consequently no need of correcting for over-cooling.

The freezing-point of water was determined each day before determining that of the solutions, and in the event of any appreciable change occurring in the atmospheric pressure during the observations on the solutions, the observation on water was repeated.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 1, July 3, 1899.

Volumetric Estimation of Zinc.—M. Pouget.—The author estimates zinc volumetrically by the method employed by MM. Rollet and Campredon for the estimation of sulphur. The zinc solution is precipitated by sulphuretted hydrogen. To the sulphide of zinc thus obtained is added a known quantity of iodine solution; the excess of the latter being titrated with thiosulphate solution, $ZnS+2I=ZnI_2+S$. The reaction is complete at the end of a few minutes. This method, however, can only be really practical if the filtration and washing of the zinc sulphide is avoided, and this is accomplished by boiling off the excess of sulphuretted hydrogen instead of filtering the zinc sulphide.

Preparation and Properties of Arsenides of Strontium, Barium, and Lithium.—P. Lebeau.—The author prepares the arsenides of calcium, barium, and strontium by the reduction of the arseniates of the alkaline earths by means of carbon at the temperature of the electric furnace. These compounds resemble, in their formulæ and their properties, nitrides and the phosphides of this group which were prepared in a state of purity by M. Moissan; for example, the action on water is similar:—

$$N_2Ca_3+6H_2O=3Ca(OH)_2+2NH_3,$$
$$P_2Ca_3+6H_2O=3Ca(OH)_2+2PH_3,$$
$$As_2Ca_3+6H_2O=3Ca(OH)_2+2AsH_3.$$

Amongst the arsenides of the metals of the alkalis, lithium arsenide is the only one which is stable enough to be prepared by the electric furnace.

Oxymethylene-cyanacetate of Methyl and some of its Homologues.—E. Grégoire de Bollemont.—The author has already described the preparation of methylic, ethylic, and amylic oxymethylenecyanacetates from the corresponding ethereal salts. He now has studied the properties of these substances, and finds that all these compounds exhibit the characteristics of strong monobasic acids, and they may be regarded as substitution derivatives of formic acid.

Use of Tetrachlorhydroquinone for the Identification and Separation of the Fatty Acids.—L. Bouveault.—When tetrachlorohydroquinone reacts with either one or two molecules of the chlorides of the fatty acids, stable compounds are formed which are well crystallised and easily purified, and so can be used for the identification of the acids, and in some cases for the separation also. The author describes the physical properties of some of compounds thus formed.

Contribution to the Study of the Bark of Rhamnus purspiana.—M. Leprince.—The author has separated and identified chrysarobin, chrysophanic acid, and emodine in the bark of the above tree.

Direct Transformation of Acetamide into Ethylamine by Hydrogenation.—M. Guerbet.—This reduction is brought about by the action of metallic sodium in the presence of boiling amylic alcohol.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxi., No. 5.

Speed and Limit of Etherification of Phosphoric Acid by Methylic Alcohol.—G. Belougou.—As the result of a series of experiments the author concludes—1. That by reacting with anhydrous phosphoric acid on methylic alcohol the limit of etherification is attained immediately. This limit is independent of the conditions under which the mixture of alcohol and acid is made. 2. Heat and time retard the coefficient of etherification, which has a minimum of about 10 per cent. 3. The presence of a small quantity of water diminishes the value of this coefficient in a very remarkable manner.

Composition of the Osmiamates.—L. Brizard.—Already inserted.

Complex Salts of Palladium: Palladoxalates.—M. Vèzes.—Already inserted.

Two New Organic Acids derived from Cyanosuccinate of Ethyl.—L. Barthe.—Two ethers are formed by acting with bromide of trimethylene on cyanosuccinate of ethyl soda. One, which is well crystallised, is saponified, and gives rise to a substance answering to the formula $C_{11}H_{16}O_8$; it melts at 159—160°, is very soluble in water, and fairly so in acetic acid, from which it eventually separates by crystallisation. The other ether, which is liquid, is treated with hydrochloric acid, and the crystalline mass obtained (which contains chlorhydrate of ammonia), together with the acid which has been formed, are treated with anhydrous ether. This solution, submitted to evaporation, leaves a crystalline residue, which is easily purified by a further crystallisation. This acid melts at 143—144°, is soluble in ether, alcohol, acetic acid, and water; it corresponds to the formula $C_8H_{12}O_6$ and is tribasic.

On the Chlorobromophenes.—V. Thomas.—In this paper the author describes some new compounds which he has obtained in a fairly pure state; and also describes the general method of the preparation of the chlorobromides, $C_6H_{(5-n)}BrCl_n$. The method consists of heating together in a flask with a reflux condenser bromide of phenyl and ferric chloride. The proportions to be used are very variable. The reactions begin at a

low temperature (about 40°) and proceed slowly. By increasing the temperature hydrochloric acid is given off in abundance, and if raised to the sublimation point of ferric chloride, the fumes are immediately reduced and ferrous chloride formed. At a high temperature, the derivatives rich in chlorine have a greater tendency to form; for it is a general fact in the whole series, that the more a compound is chlorised, the more difficult the final chlorination becomes, and thus requires more heat.

The Constitution of the Colouring-matters of the Safranine Series.— G. F. Jaubert.—The object of this paper is to answer the questions:—1. Have the safranines a symmetric constitution? 2. In the salts of safranine, such as the chlorhydrates, where is the salifiable group containing the Cl radical to be found—fixed to the azinic nitrogen, or fixed to the diazotable NH_2 radical? The author is able to reply in the affirmative to the first of these two questions; and to the second—that is, the position of the salifiable group—numerous considerations have led him to adopt the paraquinoid formula (that is, the latter one) for the red monodiazotable salts used in the arts under the name of safranine, but he reserves to himself the right to return to this important point in a future research.

Extraction and Synthesis of the Odorous Principle of Jasmine Flowers.—A. Verley.—Already noticed.

Triacetylmorphine and the Oxidation of Morphine.—H. Causse.—Already noticed.

Anabsinthine.—MM. Adrian and Trillat.—The authors describe the principal methods known for the production of absinth, and show how they differ from their own, by which they obtain anabsinthine. The principal points of difference in the two products are the following:—

	Absinthine.	Anabsinthine.
Fusing-point	68°	258—260°
Composition	$C_{15}H_{20}O_4$	$C_{18}H_{24}O_4$

A Crystallised Fibrine.—L. Maillard.—The contents of some antidiphtheritic toxine tubes were noticed after about three months to have become turbid and contain a very dense pulverulent deposit; this on examination proved to be fibrine in microscopic crystals.

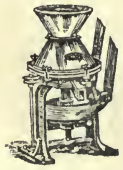
New Method for the Detection and Estimation of Acetone in Water and in Methylic and Ethylic Alcohols.—G. Denigès.—Already noticed.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Petroleum and its Products.—Will any reader kindly give the name or address of any institution in or around London where classes are held dealing with the chemistry of Petroleum and its Products.—C. H.

BRYAN CORCORAN LIM.



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ON THE WATERS OF THE SALT LAKE OF URMI.*

By R. T. GÜNTHER, M.A.,
and
J. J. MANLEY, Daubeny Curator, Magdalen College.

In June, 1897, a portion of the Government Grant was allotted to one of the authors by the Committee of the Royal Society, for the investigation of the fauna and flora of the great salt lake of Urmi, in Persia, as well as of the relations of that fauna and flora to its environment. The present research was undertaken with the view of placing on record some of the conditions prevailing in the lake at the present day.

The extraordinary changes which the level of the waters of the lake has undergone, and is still undergoing, enhance the importance of periodical examinations of the nature of the waters. The advisability of the preservation of such records was urged upon the Royal Society by its Secretary, 184 years ago. Edmund Halley, in his "Short Account of the Cause of the Saltness of the Ocean, and of the Several Lakes that emit no Rivers," expressed himself as follows:—"I recommend it therefore to the *Society*, as opportunity shall offer, to procure the Experiments to be made of the present degree of Saltness of the Ocean, and of as many of these Lakes as can be come at, that they may stand upon Record for the benefit of future Ages" (*Phil. Trans.*, 1715, vol. xxix., p. 299). At the present day there are additional reasons for recording the properties and composition of such salt lakes as are known to be inhabited by life, because Schmankewitsch (*Zeitschrift Wiss. Zoologie*, 1875, vol., xxv.), and many others of the modern school of *Entwickelungsmechanik* (Morgan, Loeb, Vernon, &c.), have proved that every change in the salinity of the waters is accompanied by definite, rapid, and corresponding changes in the anatomical structure of certain of their halophilous fauna, and especially in the species of *Artemia*, one of which occurs in Lake Urmi (Günther, *Nature*, vol. lviii., p. 435).

The superficial area covered by Lake Urmi is about 800 square miles, or about twice that of the Dead Sea. For so large an expense of water its depth is inconsiderable; the greatest soundings do not exceed 40 feet, and since much of the lake is extremely shallow, its average depth is probably under 20 feet. When viewed from the commanding heights of one of its islands, its waters show that brilliant deep blue colour which is so characteristic of salt lakes, but as seen from a boat, the light which is reflected from the light grey mud at the bottom is green.

The temperature of so small a volume of water, which is at the same time so extended as Lake Urmi, must necessarily vary considerably with the seasonable changes of temperature. During the months of July and August the temperature of the surface waters varies from 27·8° C. to 25·8° C., and the temperature of the bottom water at a depth of about 25 feet was 25° C. The specific gravity of the water, as measured on the spot by an ordinary hydrometer, was 1·11, whether the water was drawn from near the bottom or from the surface of the lake; it may therefore be assumed that the waters of the lake remote from the mouths of the fresh water tributaries were of a fairly uniform density, a result which was probably due to the thorough mixing of the waters produced by the strong south-easterly breezes prevalent at the time.

* A Paper read before the Royal Society, June 15, 1899.

The total quantity of water available for the more detailed examination was brought home in two glass wine bottles, holding about ¾ litre a-piece. The samples A and B were collected on September 16, 1898, near the base of the Bezau Daghi, on the western shore of the lake, where there is comparatively deep and clear water close in shore. The bottles were carefully corked, and it is, I think, fair to assume that no great changes have occurred in the interval between the bottling of the samples in Persia and their examination in Magdalen College Laboratory, in Oxford, seeing that the discrepancies between the analyses are very small.

The examination was both physical and chemical.

PHYSICAL EXAMINATION.

Determination of Specific Gravity.

The specific gravities of the two samples of water (A and B) were determined by Mr. H. N. Dickson, according to the method of Sprengel, with the following mean results:—

	A.	B.
Specific gravity, at 15° C. ..	1·11338	1·11389
" " 0·3° C. ..	1·11891	1·11945
Difference	0·00553	0·00556

Determination of Refractive Index.

The refractive indices (μ) were determined by means of a hollow quartz prism of 60° 6′ refracting angle, and a large spectrometer* reading to 2″ of arc. The water was at a temperature of 12·2° C. during the readings.

	A.	B.
Angle of minimum deviation of D line	25° 50′ 4″	25° 50′ 35″,
whence μ =	1·36110	1·36122

It is believed that similar optical measurements will be found to be applicable to ordinary sea waters and will be found to give a more accurate and a more readily obtained indication of the physical nature of the water than the ordinary specific gravity methods.

Determination of Boiling-point.

It has long been customary to record the boiling-points of strongly saline natural waters, but in only too many cases, owing to the lack of description of the conditions of the experiment, the records have only a small value. Many trials have convinced us that the boiling-points of brines properly determined under similar conditions yield as reliable, although less minute, information concerning the degree of salinity as specific gravity determinations.

The salt water was boiled in a platinum bottle, to which an inverted condenser containing ice-cold water was attached, in order to prevent loss of water vapour and consequent concentration. The temperature was measured by a form of platinum resistance thermometer, which reads to 0·01° C. Three readings were always taken. Firstly, the temperature of the steam from ordinary boiling water in a steam jacket and under atmospheric pressure; secondly, the temperature of the boiling salt water; and finally, the temperature of steam once more. If the first and last readings were identical, it was considered that the conditions of the experiment had remained constant. As a matter of practice it was found that when once the boiling-point of the salt water had been reached, the water continued to boil at that temperature for any length of time, so long as the pressure remained constant.

	A.	B.
Boiling-point under normal pressure	103·84° C.	103·88° C.

It will thus be seen that the three results of the physical examination of the two samples A and B are all mutually confirmatory, in so far that they indicate that

* The spectrometer which was constructed for Dr. Bedson, and the prism employed are the property of the Royal Society.

sample B had become a little more concentrated than A during its journey from Persia to Oxford.

Chemical Examination.

The method adopted was that of Dittmar, as described in the "Report on the Composition of Ocean Water" ("Challenger Reports," *Physics and Chemistry*, vol i.).

For the estimation of the lime and magnesia, 20 c.c. of the water, weighing approximately 22·2 grms., were measured off, and the quantities used in the determination of the potash and total salts were half that amount.

Examination of the Correctness of Dittmar's Factor 0·91 *for "Crude" Lime.*

Forty c.c. of the water were measured off and weighed. In accordance with Dittmar's recommendation, the calcium was precipitated as oxalate, filtered, washed, and finally weighed as oxide. The "crude" oxide obtained amounted to 0·0319 grm.: this was then re-dissolved, and again precipitated and weighed as "pure" oxide; the weight was found to be 0·0284 grm. If we multiply the weight of crude lime, 0·0319 grm., by Dittmar's factor 0·91, we obtain 0·0290 grm. as the weight of "pure" lime. This amount only differs from that actually found by +0·0006 grm., thus affording confirmatory evidence of the correctness of the factor.

The quantities of pure lime given below were determined by re-precipitation and re-purification. The magnesia was precipitated by sodium phosphate instead of by ammonium phosphate as Dittmar recommends, because when the latter reagent was used the magnesia was found to come down very slowly, and to adhere inconveniently to the sides of the vessel.

The soda was determined by the method in which all the bases are converted into normal sulphates, and the weight of the mixed sulphates is diminished by the subtraction of the weights of the potassium, calcium, and magnesium sulphates. The potash was determined by precipitation from the mixed sulphates by chloride of platinum, according to Dittmar's third and final method ("Challenger Reports," *loc. cit.*, p. 16), and his observations upon the appreciable solubility of the finely divided platinum by the cold dilute hydrochloric acid employed for washing were confirmed.

From the known amounts of lime, magnesia, and potash (see below), were deduced the following weights of normal sulphates in 100 grms. of the mixed sulphates:—

	A. Grms.	B. Grms.
Potassium sulphate	0·258	0·259
Calcium sulphate	0·146	0·171
Magnesium sulphate	1·870	1·871
Sodium sulphate (by difference)	15·547	15·606
Total sulphates	17·821	17·907

The quantities of the principal saline components dissolved in 100 grms. of the water of Lake Urmi are—

	A.	B.
Lime (CaO)	0·0603	0·0706
Magnesia (MgO)	0·6265	0·6266
Potash (K_2O)	0·1394	0·1402
Soda (Na_2O)	6·788	6·814
Chlorine (Cl)	8·496	8·536
Sulphates (SO_3)	0·6205	0·6312
	16·7307	16·8186
Oxygen equivalents of the chlorine to be deducted	1·9167	1·9258
Total salts in 100 grms. of water	14 814	14·893

Or, recalculated for 100 parts by weight of total salts, we have—

	A.	B.
Chlorine (Cl)	57·351	57 315
Sulphates (SO_3)	4·189	4·238
Lime (CaO)	0·407	0·474
Magnesia (MgO)	4·229	4 207
Potash (K_2O)	0·941	0·941
Soda (Na_2O)	45·822	45·753
Deduct [O] per [Cl_2]	−12·939	−12·931
	100·000	99·997

The hypothetical proximate composition of 100 parts of the total salts was calculated, with the following results:—

	A.	B. i.	B. ii.
Sodium chloride	86·332	86·203	86·203
Magnesium chloride	6·661	6·816	6 816
,, sulphate	4·211	4·150	3·915
Calcium sulphate	0·988	1·151	1·151
Potassium sulphate	1·741	1·741	1 741
	99·933	100·061	99·826

Result B i. was obtained by calculating the magnesium sulphate from the residual sulphate (SO_3). Result B ii. from the residual magnesium.

It is a remarkable fact that, notwithstanding the occurrence of limestone rocks and pebble beaches in the lake, no combined carbonic acid could be detected in the water; indeed, there would be no base for it to combine with. On the other hand, small quantities of free carbon dioxide were present dissolved in the water, and were estimated by Tornöe's method.*

	A.	B.
Free carbon dioxide in solution	0·028 %	0·017 %

Result A was the mean of two determinations which agreed to within 0·002 per cent, and result B was obtained twice by the use of different standard solutions; the results were identical.

No iodine or bromine could be detected in the small quantity of water available for examination.

Spectroscopic examination revealed the presence of a trace of barium. The quantity present would have been quite unweighable, and although estimated with the calcium could not have vitiated the results.

The results given under the heading B are regarded as those which most nearly represent the true condition of the lake, and consequently no attempt has been made to strike an average between the two series of results. The A results are given *in extenso*, in order to demonstrate the degree of reliability of the B results, a matter which will be of importance in the future, when, after an interval of some years, another investigation of the water of Lake Urmi is made.

City and Guilds of London Institute.—The Research Fellowships founded by the Salters' Company and the Leathersellers' Company for the encouragement of higher research in Chemistry in its relation to manufactures, tenable at the City and Guilds Central Technical College, being now vacant, the Executive Committee of the City and Guilds of London Institute will, before the commencement of next session, consider applications and elect candidates. The grant made by each of the Companies to the Institute for this purpose is £150 a year. Copies of the schemes under which the Fellowships will be awarded may be had on application to the Honorary Secretary of the Institute, Gresham College, Basinghall Street, E.C.

* Before applying Tornöe's method for the estimation of carbon dioxide to the samples of water A and B, two determinations of combined carbon dioxide in a dilute and standard solution of sodium carbonate were carried out in order to ascertain the degree of accuracy one might hope for. In the first, the carbon dioxide found only exceeded that known to be present by 0·0003 grm. and in the second by 0·0001 grm.

ON THE COMPLEX SALTS OF PLATINUM: PLATO-OXALONITRITE OF POTASSIUM.

By M. VÈZES.

WE have seen in a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 143), how the reactions which unite the plato-oxalate and the platonitrite of potassium give, as an intermediate product a mixed salt, very stable in aqueous solution, the plato-oxalonitrite of potassium, $Pt(CO_2.CO_2)(NO_2)_2K_2+H_2O$. The study of these reactions has shown that the simplest way to obtain this plato-oxalonitrite consists in causing oxalic acid to react on platonitrite of potassium. We will now describe the method which should be followed in preparing this body, starting from metallic platinum, as well as the properties of the salt formed.

I. There are two methods of preparing platonitrite of potassium from metallic platinum (*Ann. Chim. Phys.*, Series 6, vol. xxix., p. 158); in the first, the solution of the metal in aqua regia is transformed successively into chloroplatinate of potassium, then into chloroplatinite (*Bull. Soc. Chim.*, Series 3, vol. xix., p. 879), which is then treated with nitrite of potassium; the other consists in making this latter salt act directly on the chloroplatinic solution. The second of these two methods is decidedly more rapid than the other, and does not require the use of pure platinum; for these two reasons it is preferable to the former. It is true that it is more expensive, the amount of nitrite of potassium necessary being much greater; but a part of this nitrite can be, as we shall see later on, replaced by carbonate of potassium, which will greatly diminish the difference in cost of the two processes.

The method of working is as follows:—Spongy commercial platinum is dissolved in warm aqua regia. The solution is evaporated almost to dryness, and the residue taken up with warm water. Nitrous vapours are given off, and we obtain a solution of chloroplatinic acid, still containing traces of nitrated products. To this solution, diluted to about 2 litres, and heated in a large porcelain crucible, is added about 70 grms. of pure carbonate of potassium, which is thrown in in the solid state, a little at a time, while constantly agitating, to help the attack on the salt and the escape of carbonic acid. The chloro-platinic acid is thus changed into chloroplatinate of potassium, which remains in suspension in the solution. To this mixture, which must be boiled and to which water must be added from time to time to maintain its volume, we gradually add pure solid nitrite of potassium. This salt is dissolved with a slight disengagement of nitrous fumes, and the resulting liquid gradually re-dissolves all the chloroplatinate in suspension, so as to give finally an almost clear liquid of a greenish-yellow colour with a distinctly alkaline reaction. This result is attained by using about 350 grms. of pure commercial nitrite of potassium containing about 80 per cent of actual nitrite, though a little more than is required by the equation showing the transformation of the chloroplatinate into the platonitrite—

$$PtCl_6.K_2+6NO_2K=Pt(NO_2)_4K_2+2NO_2+6KCl.$$

The solution thus obtained, freed by filtration from the slight precipitate which it might contain (oxides of the commoner metals, double potassic nitrites of iridium and rhodium), is left to cool; it gives an abundant deposit of anhydrous platonitrite, which is drained and re-crystallised in boiling water. This re-crystallisation gives about 200 grms. of the hydrated platonitrite, $Pt(NO_2)_4K_2+2H_2O$.

The salt thus obtained is then re-dissolved in about 2 litres of warm water, and an excess (100 grms.) of crystallised oxalic acid is added. On boiling, the acid is dissolved, colouring the liquor green, and abundant nitrous fumes are given off. When this ceases and the solution becomes yellow it is allowed to cool, and the oxalonitrite crystallises out. We thus obtain by the first operation about 160 grms. of very pure salt; the mother-liquor conveniently concentrated will still give another 50 grms.

II. The salt thus prepared is in the form of bright yellow prismatic crystals. Under the microscope these crystals have the general appearance of a parallelogram of which the acute angle is about 68°; they act on polarised light, and have a position of extinction about 25° from one of the sides of the parallelogram.

The crystallographic examination of this salt, kindly made by M. Goguel, has given the following results:—

The crystals are monoclinic, citron-yellow, transparent, brilliant, and with very distinct facets; they are elongated along the zone $h'(100)$ $g'(010)$, and flattened along g'. They present the facets g' dominant, $m(110)$, $p(001)$, $e^{\frac{1}{2}}$ (011), $a'(\bar{1}01)$. Their dimensions are from 3 to 4 m.m. in length, 2 m.m. wide, and about ½ m.m. thick.

Angles.		Measured.	Calculated.
$m\,g'$	$(110)\,(010)$ ..	66° 2′	
$m\,n$	$(1\bar{1}0)\,(110)$ ..	47° 56′	47° 56′
$g'\,e'$	$(010)\,(011)$ ..	70° 6′ 10″	70° 14′
$e'\,p$	$(011)\,(001)$ ..	19° 54′ 55″	19° 46′
$g'\,p$	$(010)\,(001)$ ..	90° 1′ 5″	90°
$m\,e'$	$(110)\,(0\bar{1}1)$ ..	63° 27′ 45″	63° 27′ 25″
$e'\,a'$	$(0\bar{1}1)\,(\bar{1}01)$ ..	50° 51′ 50″	
$a'\,m\,adj$	$(\bar{1}01)\,(\bar{1}10)$ ..	63° 41′ 15″	
$p\,a'$	$(001)\,(\bar{1}01)$ ..	47° 52′ 51″	
$p\,h'$	$(001)\,(100)$ ..	47° 52′ 51″	68° 20′ 9″

These measurements lead to the parameters:—

$$a:b:c::0{\cdot}4131:1\,.\,0{\cdot}3340,$$
$$\beta=111°\,39'\,51''.$$

If we examine the optical properties in the plane g' we observe that the plane of the optical axes is perpendicular to g', making an angle of about 25° with the direction $h'g'$ in the obtuse angle ph'. These axes are very wide apart, their acute bisectrix appears to be in g'.

When dried in the cold by compression between filter papers the plato-oxalonitrite of potassium is undecomposed in the air.

Heated to 100° it effloresces and loses a molecule of water of crystallisation. This dehydration is rather slow; if we do not exceed 110° we may have to go on heating for several days before obtaining a residue of a constant weight. It is much more rapid at about 130°.

If we continue to raise the temperature of the salt thus dehydrated, a very lively reaction becomes manifest at about 240°. At this point a sort of boiling takes place, which soon permeates the whole mass, and the salt, which was of a greyish colour since it began to effloresce, rapidly changes to black. The gas given off in this transformation, and which causes this boiling up, is entirely composed of carbonic acid, and does not contain a trace of nitrous fumes. As for the black residue, it is formed of platinum and nitrite of potash. This destruction of the plato-oxalonitrite by heat should therefore be according to the formula $Pt(CO_2.CO_2)(NO_2)_2K_2=Pt+2NO_2K+2CO_2$, an equation which is justified by the figures quoted further on when dealing with the analysis of this salt.

The plato-oxalonitrite, though not very soluble in cold water, becomes much more so as the temperature rises; in fact it dissolves in seven times its weight of boiling water, and in sixty times its weight of cold water. It is thus much less soluble in the cold than the plato-nitrite, which requires twenty-seven times its weight of water at 15°. Consequently it is still more easily purified by re-crystallisation than the platonitrite.

This slight solubility in cold water is susceptible of an important application. When we effect the separation of the platinum metals by the nitrite method (A. Joly and E. Leidié, *Comptes Rendes*, vol. cxix., p. 1259), the platinum is separated from the allied metals in the form

TABLE I.

	Calculated.		Found.					
			I.	II.	III.	IV.	V.	VI.
Pt	194·8	41·34	—	41·57	41·55	41·33	41·06	41 64
2K	78·3	16·62	—	16·50	16·57	—	16 64	16·60
2C	24·0	5·09	—	—	—	5·09	—	—
2N	28·1	5·96	—	—	—	5·95	—	—
8O	128·0	27·17	—	—	—	—	—	—
H_2O	18·0	3·82	3·92	3·60	3·84	—	—	—
$Pt(CO_2.CO_2)(NO_2)_2K_2+H_2O$	471·2	100·00	—	—	—	—	—	—
$Pt+2NO_2K$	365·2	77·50	77·44	77·88	77·70	—	—	78·07
$Pt+SO_4K_2$	369·1	78·33	—	78·30	78·43	—	78·10	78·59
$2CO_2$	88·0	18 68	18·64	18·52	18·46	18·65	—	—

TABLE II.

	Calculated.		Found.				
			I.	II.	III.	IV.	V.
Pt	194·8	41·34	41·81	41·64	—	—	—
2K	78·3	16 62	16·25	16·49	—	—	—
2C	24·0	5·09	—	—	5·58	5·50	5·35
2N	28·1	5·96	—	—	5·75	5·58	5·73
8O	128·0	27·17	—	—	—	—	—
H_2O	18·0	3·82	—	—	3·89	—	—
$Pt(CO_2.CO_2)(NO_2)_2K_2+H_2O$	471·2	100·00	—	—	—	—	—
$Pt+2NO_2K$	365·2	77·50	77·25	77·80	—	—	—
$Pt+SO_4K_2$	369·1	78·33	77·99	78·34	—	—	—
$2CO_2$	88·0	18·68	—	—	20·44	20·15	19·61

of platonitrite of potassium. The transformation of this salt into the oxalonitrite, still more soluble in the cold, enables us to obtain this metal in a much purer state; and the decomposition by heat of this oxalonitrite, followed by several washings with warm water, enables us to immediately recover the metal. If we take the precaution to pulverise the oxalonitrite very finely before submitting it to the action of heat, we should obtain pure platinum in a very fine state of division, and consequently in a very convenient form for studying the reactions of this metal.

The aqueous solution of the oxalonitrite is very stable; like that of the platonitrite, it can be boiled and evaporated to dryness without decomposing the salts it contains.

Oxalonitrite of potassium is insoluble in alcohol.

III. The methods formerly employed for the analysis of the complex nitrated salts of platinum (*Ann. Chim. Phys.*, Series 6, vol. xxix., p. 149-158), are applicable without much modification to the case of the plato-oxalonitrite and its derivatives.

The estimation of the carbon is made in the state of carbonic acid gas, of which the volume is measured at the same time as that of the nitrogen (*loc. cit.*, p. 150), with the aid of a column of cupric oxide in the combustion tube.

The estimation of the platinum and the potassium is effected by heating the salt to about 300°; this eliminates all the carbon in the state of carbonic acid gas. This operation is carried out over a Bunsen burner, the small porcelain crucible in which the analysis is carried out being covered with a small watch-glass, by which all loss from projection is avoided. Its use further enables us to control the estimation of the water of crystallisation; if the dehydration is not complete traces of water retained by the salt will show on the surface of the glass. The residue from this calcination, consisting of platinum and nitrite of potassium, is then treated with a slight excess of dilute sulphuric acid, then evaporated to dryness and calcined in an atmosphere of carbonate of ammonium. The estimation is completed as has already been described (*loc. cit.*, pp. 155 and 157, Method VI.).

Analysis of the Plato-oxalonitrite.—The formula $Pt(CO_2.CO_2)(NO_2)_2K_2+H_2O$, attributed above to the material dried in the cold between filter papers, results from the following analyses. The analyses I., II., III., and IV. were performed on material obtained by the platonitrite and oxalic acid; analysis V. on a product obtained by the plato-oxalate and nitrite of potassium (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 146); analysis VI., on a product obtained by the plato-dichloronitrite, and the neutral oxalate of potassium (*loc. cit.*, p. 147).

I. 1·1926 grms. of material, heated to 110°, lost 0·0468 grm. of water; the dry product, heated to about 300°, lost 0·2223 grm. of carbonic acid, leaving a residue of 0·9235 grm.

II. 1·1143 grm. of material, heated to 110°, lost 0·0401 grm. of water; the dry product, heated to about 300°, lost 0·2064 grm. of carbonic acid, leaving a residue of 0·8678 grm., which, heated to redness with an excess of sulphuric acid, gave 0·4632 grm. of platinum and 0·4093 grm. of sulphate of potassium, containing 0·1839 grm. of potassium.

III. 0·8651 grm. of material, heated to 110°, lost 0·0329 grm. of water. The dry product, heated to about 300°, lost 0·1580 grm. of carbonic acid, leaving a residue of 0·6652 grm., which, heated to redness with an excess of sulphuric acid, gave 0·3557 grm. of platinum and 0·3157 grm. of sulphate of potassium (containing 0·1418 of potassium).

IV. 1·5381 grms. of material, heated to redness with an excess of tungstic acid, gave 73 c.c. of nitrogen at 0° and 760 m.m. (weighing 0·0916 grm.), and 146 c.c. of carbonic acid at 0° and 760 m.m. (weighing 0·2869 grm., and containing 0·0782 grm. of carbon). The contents of the boat, after dissolving the tungstic acid in an alkali, gave 0·6357 grm. of platinum.

V. 0·5631 grm. of material, heated to redness with an excess of sulphuric acid, gave 0·2312 grm. of platinum and 0·2086 grm. of sulphate of potassium (containing 0·0937 grm. of potassium).

VI. 0·3115 grm. of material, heated to 300°, left a residue of 0·2432 grm., which, heated to redness with an excess of sulphuric acid, gave 0·1297 grm. of platinum and 0·1151 grm. of sulphate of potassium (containing 0·0517 grm. of potassium). (See Table I.).

Analysis of the Greenish Salt.—Below we give the analysis of the greenish crystals, the production of which has already been described (*Bull. Soc. Chim.*, Series 3, xxi., p. 145)—analyses from which we may conclude that these green crystals are plato-oxalonitrite modified in appearance by admixture with a small quantity of plato-oxalate. In fact we have found a little more carbon and a little less nitrogen than would be contained by the normal plato-oxalonitrite. The Analyses I., II., III., and IV. were carried out on products obtained by the plato-nitrite and an excess of oxalic acid; the Analysis V. on a product obtained by treating the dark coloured plato-oxalate of potassium with a small quantity of nitrite of potassium (*loc. cit.*, p. 146).

I. 0·6786 grm. of material, heated to about 300°, left a residue of 0·5242 grm., which, heated to redness with an excess of sulphuric acid, furnished 0·2837 grm. of platinum and 0·2455 grm. of sulphate of potassium (containing 0·1103 grm. of potassium).

II. 0·5171 grm. of material, heated to about 300°, left a residue of 0·4023 grm., which, heated to redness with an excess of sulphuric acid, furnished 0·2153 grm. of platinum and 0·1898 grm. of sulphate of potassium (containing 0·0853 grm. of potassium).

III. 0·5711 grm. of material, heated to 120°, lost 0·0222 grm. of water. The dry residue, heated to redness with tungstic acid, gave 26·2 c.c. of nitrogen at 0° and 760 m.m. (weighing 0·0329 grm.), and 59·4 c.c. of carbonic acid at 0° and 760 m.m. (weighing 0·1167 grm. and containing 0·0318 grm. of carbon).

IV. 0·5276 grm. of material, heated to redness with tungstic acid, gave 23·5 c.c. of nitrogen at 0° and 760 m.m. (weighing 0·0294 grm.), and 54·1 c.c. of carbonic acid at 0° and 760 m.m. (weighing 0·1063 grm. and containing 0·0290 grm of carbon).

V. 0·6534 grm. of material, heated to redness with tungstic acid, gave 29·9 c.c. of nitrogen at 0° and 760 m.m. (weighing 0·0375 grm.), and 65·2 c.c. of carbonic acid at 0° and 760 m.m. (weighing 0·1281 grm., and containing 0·0349 grm. of carbon). (See Table II.).—*Bull. Soc. Chim.*, Series 3, xxi., No. 10.

A VOLUMETRIC METHOD FOR THE ESTIMATION OF BORIC ACID.*

By LOUIS CLEVELAND JONES.

When boric acid and mannite are mixed in solution, a peculiar compound of strongly acid properties is the result. This compound decomposes carbonates, and its acid taste is comparable to that of citric acid, much stronger than that of boric acid alone. Magnanini (*Gaz. Chim*, xx., 428-440; xxi., 134-145) has found that the product of such a mixture of boric acid and mannite solutions shows greater electrical conductivity and a lower freezing-point than a similar molecular solution of either substance alone. Other polyatomic alcohols (but all to a less degree than mannite) and some organic acids show this peculiar property of combining chemically with boric acid to increase its acid qualities (Klein, *J. Pharm. Chem.*, [4], vol. xxviii.; Lambert, *Compt. Rend.*, cviii., 1016, 1017). Of this reaction between boric acid and the polyatomic alcohols, Thomson (*J. S. C. I.*, xv., 432), Barthe (*J. Pharm. Chim.*, xxix., 163), and Jörgensen (*Zeitschr. f. Angew. Chem.*, 1897, 5) have taken advantage to develop methods for the volumetric estimation of boric acid. Glycerin is used to form a combination with boric acid, sufficiently acidic to give an acid reaction when used with a sensitive indicator and make possible its titration with an alkaline solution. Hönig and Spitz (*Zeitschr. f. Angew. Chem.*, 1896, 549) show that in the method of Jörgensen a very large amount of glycerin must be used to prevent the appearance of the indication of alkalinity with phenolphthalein before all the boric acid is neutralised according to the following equation:—

$$2NaOH + B_2O_3 = 2NaOBO + H_2O;$$

that in the presence of carbonates the solution must be boiled to decompose bicarbonates, and the escape of boric acid by volatilisation prevented by the use of a return condenser; and that silica must be removed by the process of Berzelius, and the solution then neutralised by the use of methyl orange before a titration of the boric acid can be made.

Vadam (*J. Pharm. Chim.* [6], viii., 109-111), for the estimation of boric acid in butter, makes use of mannite, which, as he finds, gives sharper indication with litmus than glycerin. According to this process, the solution to be analysed for boric acid is neutralised by the use of litmus and a solution of sodium hydroxide. Mannite (1—2 grms.) is then added, bringing about an acid reaction with the boric acid present in free condition. The solution is then titrated to alkalinity by sodium hydroxide.

None of the above methods with glycerin have, in my experience, given anything but comparatively crude results. The weak acidic properties of boric acid, the interference (and difficulty of removal) of carbon dioxide with all organic indicators sufficiently delicate to be used with boric acid, and, indeed, the procuring of a standard alkali containing no carbonate, together with the supposed detrimental influence of silica and the lack of a convenient method for its removal, have made the process of Gooch (*Amer. Chem. Journ.*, ix., 23-33; Moissan, *Compt. Rend.*, cxvi., 1087; Kraut, *Zeitschr. f. Anal. Chem.*, xxxvi., 165; Montemartini, *Gaz. Chim. Ital.*, xxviii., 1, 344), which involves distillation and weighing with calcium oxide, the only means (though requiring long time and exceeding care) in use for the accurate separation and estimation of boric acid. Recently sodium tungstate has been recommended from this laboratory (Gooch and Jones, *Amer. Journ. of Science*, vii., 34) as a substitute for calcium oxide to retain the distilled boric acid. The entire process, however, is one of the most exacting in analytical chemistry, and for this reason a convenient, rapid—and at the same time accurate—method for the estimation of boron is especially desirable. The first step toward the development of such a process must be the convenient preparation and the accurate estimation of the standard solution of alkali to be used for neutralising the boric acid. This has been found to be easily accomplished by the process recommended by Küsler (*Zeitschr. f. Anorg. Chem.*, xiii., 124-150). This observer, in an extensive investigation of the analytical methods for the volumetric estimation of alkalinic and alkali carbonates in solution, finds that both phenolphthalein and methyl orange are appreciably sensitive to carbonic acid; but when this interfering agent is removed by precipitation with barium chloride according to the process of Winkler (Mass-analyse), the remaining free alkali may be estimated with great accuracy by phenolphthalein and decinormal hydrochloric acid.

Obviously, if the difficulties dependent upon the action of carbon dioxide can be obviated, and if the acidity of the boric acid can be increased to such an extent that a sufficiently sensitive indicator will give with accuracy the neutralisation-point with free alkali, and if the alkali and stronger acid can be combined while boric acid alone remains free, then it should be possible to estimate boric acid volumetrically. Experiment has shown that barium chloride removes carbon dioxide, and that mannite makes a combination with boric acid strongly acidic to phenolphthalein.

To obtain the boric acid alone in free condition many attempts have been made. Gladding (*Journ. Am. Chem. Soc.*, iv., 568), Thaddeeff (*Zeitschr. f. Anal. Chem.*, xxxvi., [9], 568), and Rosenbladt (*Zeitschr. f. Anal. Chem.*, xxvi., 18) have isolated the boric acid by distillation with methyl

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. vii., February, 1899.

alcohol and a non-volatile acid. Many indicators theoretically insensible to free boric acid have been used to indicate the neutralisation of the stronger acids. Hönig and Spitz (*Zeitschr. f. Anorg. Chem.* [18], 549) and Thomson (*J. S. C. I.*, xv., 432) use methyl orange, Morse and Burton (*Am. Chem. Journ.*, x., 154) tropæolin oo, while Vadam (*J. Pharm. Chim.*, [6], viii., 109-111) makes use of litmus. All these indicators, however, have been found by experiment to be more or less affected by boric acid in solution. On the other hand, I have found in the well-known reaction, according to which a stronger acid liberates regularly iodine from a mixture of iodide and iodate, the solution of this difficulty. If both the iodide and iodate are in excess of the acid the entire amount of free acid will be neutralised, and the corresponding amount of iodine liberated according to the following equation: —

$$5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + 3I_2.$$

This liberated iodine may be removed by sodium thiosulphate, and a solution obtained which is absolutely neutral, containing only neutral salts, potassium iodide, iodate, and tetrathionate. The statements made by P. Georgevic (*J. Prac. Chem.*, xxxviii., 118) and Furry (*Am. Chem. Journ.*, vi., 341), that boric acid present in moderate amount in solution has not the slightest action on a mixture of iodide and iodate, have been experimentally verified. Therefore when this acid is liberated by an excess of a stronger acid, and the iodine set free destroyed by thiosulphate, it remains free in solution to be titrated in any convenient matter possible.

Following along the lines suggested by the above reactions, a volumetric process for the estimation of boric acid has been developed. For a basis of the investigations, a standard solution of boric acid was prepared by dissolving in a litre of water about 8 grms. of carefully weighed anhydrous boric oxide. This anhydrous boric oxide was prepared from the several times re-crystallised hydrous boric acid by long-continued fusion over a blast-lamp. A solution of approximately *n*/5 sodium hydroxide was prepared from the ordinary sodium hydroxide of the laboratory. The free alkali in this solution was estimated by the process of Winkler recommended by Küsler. The acid used to make this estimation was hydrochloric, standardised by silver nitrate.

The full method for the estimation of boric acid as finally elaborated is as follows:—The solution is made clearly acid to litmus by hydrochloric and 5 c.m.³ of a solution (10 per cent) of barium chloride added. An amount of iodate and iodide of potassium sufficient to liberate an amount of iodine at least equivalent to the excess of hydrochloric acid in the acidified solution is mixed with starch in a separate beaker, and the iodine, which is usually thrown out by this mixture, is just bleached by a dilute solution of thiosulphate.

To the now neutral solution of iodide and iodate a single drop of the solution to be analysed is transferred by a glass rod. If a blue colouration is developed, the solution is acidic with hydrochloric acid, and all the boric acid is in free condition. The amount of iodide and iodate used depends upon the acidity of the solution containing boric acid. Usually 10 c.m.³ of a 25 per cent solution of iodide and the same amount of a saturated solution of iodate is sufficient. Any larger excess of hydrochloric acid should be neutralised by sodium hydroxide before the iodide and iodate mixture is added. After the addition of the iodide and iodate solution, containing starch, to the boric acid solution, the liberated iodine should be carefully bleached by thiosulphate. Any excess of thiosulphate in reasonable amount does not seem to be detrimental, but in practice the starch iodide colour is clearly bleached, and no more then added. Carbonates prevent a definite indication of the neutral point by thiosulphate and starch iodide, therefore the barium chloride (about 5 c.m.³) should be added before this point in the process. The mixture of iodide and iodate is not added to the solution to be analysed until after it is made acidic, for the reason that when the neutral point is approached by the addition of hydrochloric acid, the starch iodide is thrown out locally by the acid, and the small amount of sodium borate remaining undecomposed does not again bleach the colouration produced, thus obscuring the neutral point which must be obtained before titrating for boric acid.

The solution after the bleaching of the iodine by thiosulphate is colourless, and contains only starch, neutral chloride, potassium tetrathionate, iodide and iodate, and all the boric acid present in uncombined condition. The carbonate lies out of the sphere of action in insoluble form as barium carbonate. A few drops of the indicator, phenolphthalein, are now added, and the alkaline solution run in until a strong red colouration is produced. A pinch of mannite is then added, which bleaches the phenolphthalein colouration, and the alkali solution again run in to a faint indication, which, if permanent on the addition of more mannite, may be taken as the reading-point. About 1—2 grms. of mannite are necessary for a determination. The boro-mannite compound is sufficiently acidic to liberate iodine abundantly, but it appears to be a time reaction, and at the end of six hours only about 95 per cent of the theoretical amount (considering B_2O_3 as a bivalent acid) has been thrown out. The combination of boric acid and mannite liberates in the presence of iodide and iodate immediately only about one-half the iodine required on the theory that B_2O_3 under these conditions acts as a bivalent acid, or with the neutralising power of metaboric acid, HOBO. When no mannite is present phenolphthalein gives an alkaline indication when only about one-half the amount of alkali theoretically necessary to form the metaborate, NaOBO, has been added. Obviously, then, the starch iodide colouration will not appear at all on the addition of mannite, if about one-half the free boric acid is first neutralised by the solution of alkali, and the remainder of the alkali immediately added to complete neutralisation. The point at which the danger of the appearance of the iodide colouration on the addition of mannite has been passed, is roughly indicated before the mannite has been added by the appearance of the strong alkaline indication of phenolphthalein. This indicator would not need to be added at all, if the boro mannite compound quickly and regularly liberated iodine from the iodide and iodate. The fact, however, that this compound of boric acid and mannite—as has been ascertained by experiment, liberates, on standing twelve hours, about 99 per cent of the theoretical amount of iodine, places the strength of this acid above that of citric or tartaric acid as investigated by Furry (*Am. Chem. Journ.*, vi., 341). With phenolphthalein, however, the end reaction is sharp, and the small amount of carbonate present in the standard solution of alkali is precipitated by the barium chloride already in the solution. The calculation must therefore be based on the amount of free hydroxide in the standard solution of alkali used, according to the following representation:—

$$B_2O_3 + 2NaOH = 2NaOBO + H_2O.$$

The best results and the most definite indications are obtained in cold solution of a volume not greater than 50 c.m.³. This fact accords with the observations of Magnanini (*Gaz. Chim.*, xx., 428, and xxi., 134), that the relative electrical conductivity of the boro-mannite solution is decreased by dilution and elevation of the temperature. When silicates are present in solution the silicon dioxide is liberated by the excess of hydrochloric acid, and this oxide, whether in hydrous or anhydrous condition, neither affects the indication with iodine nor phenolphthalein, nor does it form with mannite a compound of acidic properties. Ammonium salts interfere with the indication given by phenolphthalein, and may be removed by boiling with potassium hydroxide in excess, or an indicator used not affected by them.

To test the action of fluorides in the process, several experiments were made in which hydrofluoric acid (10 c.m.s of *n*/10 solution) was introduced into the solution containing salts of sodium, free hydrochloric and boric acids. Barium chloride was then added, and the analysis for boric acid completed in the usual way without the accuracy of the results being in any way interfered with by the presence of hydrofluoric acid.

The following table contains the results of a series of analyses in which the boric acid was first drawn into an excess of sodium hydroxide, then estimated according to the method described.

The standard solutions of boric acid used contained—I., 7·153 grms., and II., 7 706 grms. per litre. The solution of free sodium hydroxide was 0·21427 normal.

Table I.

		B_2O_3 Sol. taken.	NaOH Sol. required	B_2O_3 taken.	B_2O_3 found.	Errors on B_2O_3.
		C.m.s.	C.m.s.	Grm.	Grm.	Grm.
I.	1.	21·95	21·02	0·1571	0·1577	+0·0006
	2.	20·68	19·65	0·1479	0·1474	−0·0005
	3.	20·73	19·63	0·1483	0·1473	−0·0010
II.	4.	23·05	23·71	0·1776	0·1777	+0·0001
	5.	23·10	23·80	0·1780	0·1783	+0·0003
	6.	22·76	23·35	0·1754	0·1750	−0·0004
	7.	24·08	24·78	0·1855	0·1857	+0·0002
	8.	22·00	22·50	0·1695	0·1686	−0·0009
	9.	20·78	21·28	0·1601	0·1595	−0·0006

Practical tests of the method were made upon specimens of crude calcium borate and colemanite.*

The finely-ground minerals were dissolved in hydrochloric acid, and the analyses proceeded with as above described.

Analysis of Crude Borate of Lime.

Table II.

	Ca borate taken.	B_2O_3 found.	B_2O_3 in per cent.
	Grm.	Grm.	
1.	0·4016	0·2289	56 99
2.	0·4044	0·2302	56·92
3.	0·4000	0·2285	57·11

Analysis of Colemanite.

Table III.

	Mineral taken.	B_2O_3 found.	B_2O_3 p.c.	
	Grm.	Grm.		
1.	0·4034	0·2064	51·15	
2.	0·4070	0·2069	50·80	
3.	0·6004	0·3054	50·86	Average.
4.	0·6006	0·3056	50·89	50·99 %
5.	0·5059	0·2592	51·24	
6.	0·5092	0·2592	50·89	

An analysis for boric acid by this process can be completed in five minutes, and the results are obviously accurate within the limits of ordinary analysis.

The usually interfering substances, fluorine, silica, and carbon dioxide, have no detrimental influence on the results of this process.

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF COPPER.†

By RICHARD K. MEADE.

The average analyst is often deterred from the use of a volumetric method by the necessity of making and standardising a special solution. In many cases it takes nearly as much time to ascertain the strength of the required solution as it does to make the analysis itself, and the standardisation and analysis together render the volumetric method frequently as slow, if not slower, and vastly more troublesome than the gravimetric determination.

Volumetric analysis, therefore, becomes more and more an ideal method of quantitative determination as it approaches the requirement of a single standard solution, capable of having its strength accurately determined by simple means, giving a single, definite, clear-end reaction.

In iron and steel laboratories permanganate is fast coming to the front as a help to rapid analysis. Iron, phosphorus, manganese, sulphur (Payne's iodine solution is prepared by adding standard permanganate to potassium iodide), and calcium can all be quickly determined by the use of one standard solution. While it may never be possible to supplant other standard solutions by permanganate, still the sphere of its usefulness is a large one and is constantly enlarging.

For a year or more I have been experimenting upon a new method for the determination of copper by permanganate, which seems to possess many points of superiority over the old one of reduction by grape-sugar. In general it is as follows:—The copper is brought into solution as a sulphate, either by dissolving it in sulphuric acid or evaporation of its solution with sulphuric acid. The greater part of the free acid is neutralised by ammonia, the solution warmed, sulphurous acid added until the solution smells strongly of the reagent, and then a slight excess of ammonium or potassium thiocyanate (Rivot, *Compt. Rend.*, xxxviii., 868; and Busse, *Zeitschr. Anal. Chem.*, 1878, 55). The copper is immediately precipitated as cuprous thiocyanate. Stirring and warming renders the precipitate heavy and easily handled. The solution is filtered through asbestos, using the pump, and well-washed. The precipitate and filter are thrown into the beaker in which the precipitation was made and heated with a solution of caustic soda or caustic potash. Double substitution takes place. Hydrated cuprous oxide and potassium or sodium thiocyanate result:—

$$2CuSCN + 2KOH = Cu_2(OH)_2 + 2KSCN.$$

The oxide is filtered on asbestos and washed well with hot water. The precipitate and filter are again placed in the same beaker and an excess of ferric chloride or ferric sulphate (free from nitric acid, free chlorine, or ferrous salts), together with a little dilute sulphuric acid, added. The copper oxide reduces a corresponding amount of iron from the ferric to the ferrous condition:—

$$Cu_2O + Fe_2Cl_6 + 2HCl = 2CuCl_2 + 2FeCl_2 + H_2O.$$

The beaker is warmed and stirred until all the copper oxide is dissolved. The solution is then poured through a perforated platinum disk, and the asbestos which stays behind upon it washed with water, to which has been added a little sulphuric acid and a little ferric chloride or sulphate. The solution is then titrated with permanganate. The iron equivalent to the permanganate used multiplied by 1·125 gives the weight of copper in the sample.

Instead of sulphurous acid, ammonium or sodium bisulphite may be used to reduce the copper. A solution of equal weights of sodium bisulphite and potassium thiocyanate answers well as a reagent for the precipitation of the metal. Since copper is the only metal precipitated by an alkaline thiocyanate from an acid solution, the presence of arsenic, antimony, bismuth, zinc, and other materials which render the electrolytic, the cyanide, and the iodine method inaccurate, will not affect the results.

The caustic alkali solution, used to convert the cuprous thiocyanate into cuprous hydroxide, must not be too strong, or some of the metal will go into solution, colouring the liquid blue. I have used about a half normal solution of caustic potash, made by dissolving 28 grms. of the salt in a litre of water. Either ferric sulphate or ferric chloride may be used to dissolve the cuprous oxide. The former is probably the safest, but

* These specimens were kindly furnished by Dr. C. A. Crampton, of Washington, whom I desire to thank for this courtesy.

† Contribution from the Chemical Laboratory of Lafayette College. From the *Journal of the American Chemical Society*, vol. xx., No. 8.

the latter appears to dissolve the precipitate the more readily of the two.

As a test of the accuracy of the method 4 grms. of pure electrolytic copper were dissolved in nitric acid and the solution evaporated with sulphuric acid until the nitric acid was expelled. The solution was cooled and diluted to 1 litre. The copper contained in 50 c.c. was then determined electrolytically with the following result:—

	Grm.
1.	0·2003
2.	0·2003
3.	0·2000
4.	0·1997
Average	0·2001

The copper in 50 c.c. was next determined by the thiocyanate-permanganate method outlined above. The permanganate solution used was made by dissolving 5·02 grms. of pure crystallised potassium permanganate in water, and diluting, after standing twenty-four hours, to 2 litres. Its strength was determined by titration against iron wire and against ferrous ammonium sulphate.

Against ferrous ammonium sulphate:—

	Grm. iron.
1. One c.c. =	0·004455
2. One c.c. =	0·004456

Against iron wire:—

	Grm. iron.
3. One c.c. =	0·004460
4. One c.c. =	0·004449
Average one c.c. =	0·004455

One c.c. = 0·004455 × 1·125 = 0·005012 grm. copper.

Below are the results on 50 c.c. of the copper solution containing 0·2001 grm. copper by the thiocyanate permanganate method:—

No.	Permanganate. C.c.	Copper. Grm.
1.	39·6	0·1985
2.	39·5	0·1980
3.	39·6	0·1985
4.	39·7	0·1990
5.	40·0	0·2004
6.	39·8	0·1995

In determinations numbers 1, 5, and 6, ferric chloride was used to dissolve the cuprous oxide; in numbers 2, 3, and 4, ferric sulphate was used.

As a further and more practical test of the method, the copper in some samples of copper ore was carefully determined by the electrolytic, and then by the thiocyanate-permanganate method. Below are the comparative results:—

Sample.	Weight of sample.	Permanganate.	Copper by thiocyanate-permanganate method.	Copper by electrolytic method.
	Grm.	C.c.	Per cent.	Per cent.
1. Chalcopyrite I.	1·0	39 6	19·85	19·95
2. ,,	1·0	39·3	19·70	19·86
3. Chalcopyrite II.	2 0	24·6	6 16	6 37
4. ,,	2·0	24·8	6·21	6·30
5. Malachite ..	1·0	72·2	36 19	36·10
6. ,, ..	1·0	72·2	36·19	36·15
7. Tetrahedrite ..	1·0	42·0	21 05	21·06
8. ,, ..	1·0	41 7	20·90	21·18

It will be seen by the above results that the method is accurate enough for ordinary commercial purposes. In spite of its three filtrations the method is quite rapid. Not counting the time required for the solution of the ore duplicate analyses can be easily made in from a half to three-quarters of an hour.

In the writer's opinion the process is superior to both the iodine and the cyanide method. It requires the use of no rapidly changing solutions, but one which every analyst has on hand nearly all the time. The end reaction is clear, distinct, and familiar to all chemists. The method is applicable to any ore, matte, or alloys. It is as rapid as the cyanide, except in certain cases favourable to the latter, and more rapid than the iodine method. Finally, not the least of its points of advantage is that it is more accurate than either of the two.

ON A TEST, BY THE FREEZING-POINT METHOD, OF THE IONISATION COEFFICIENTS DETERMINED BY THE CONDUCTIVITY METHOD, FOR SOLUTIONS CONTAINING POTASSIUM AND SODIUM SULPHATES.*

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(Continued from p. 59).

Observed and Calculated Values of the Depression of the Freezing-point for Simple Solutions.

THE following table contains the observations of the depression of the freezing-point of simple solutions, together with observations on solutions of about the same concentration by Loomis (*Phys. Review*, 1896, iii., 277) and Jones (*Zeit. Phys. Chem.*, 1893, xi., 536) for comparison. The depressions are expressed in centigrade degrees.

TABLE III.

Concentration gr.-eq. / litre.	Depression of Freezing-point. K_2SO_4.	Depression of Freezing-point. Na_2SO_4.	Observer.
0·03949	0·0975	—	Jones.
0·04	0·0952	0·0974	Loomis.
0·050	0 1185	0·1191	Author.
0·055	0·1296	0·1304	,,
0·0579	0·1397	—	Jones.
0·060	0·1407	0·1416	Author.
0·070	0·1629	0·1638	,,
0·07556	0·1792	—	Jones.
0·080	0·1851	0·1856	Author.
0·10	0·2307	—	Jones.
0·10	0·2271	0·2297	Loomis.
0·100	0·2285	0·2286	Author.
0·116	0·2655	—	Jones.
0·19685	0·42525	—	,,
0·20	0·4317	0·4340	Loomis.
0.200	0·4322	0·4330	Author.
0·250	0·5295	0·5300	,,
0·300	0·6240	0·6252	,,
0·350	0 7196	0·7157	,,
0·40	0·8134	0·8141	Loomis.
0·400	0·8128	0·8100	Author.
0·450	0·9063	0·8968	,,
0·500	0 9950	0·9875	,,
0·60	1·1672	1·1604	Loomis.
0·600	1·170	1·155	Author.
0·700	1·341	1·323	,,

It will be seen, especially if the above results be plotted, that all three sets of observations agree very well with one another, but that mine agree better with Loomis's than with those of Jones. Their agreement with Loomis's is very close.

The following table contains the observed and calculated values of the freezing-point depressions for simple solutions, with the differences expressed as percentages of the observed values. In the calculations van 't Hoff's

* From the *Transactions of the Nova Scotian Institute of Science*, vol. x., Session 1898-99.

constant was taken to be 1·86, and the expression used for the depression was—

$$\Delta = 1{\cdot}86\ (1+2a)\ N/2,$$

where N is the concentration of the solution in gr.-equivalents per litre.

TABLE IV.—*Depression of Freezing-point.*

Concentration (gr.-eq.)/1.	Potassium sulphate solutions. Observed.	Calculated.	Diff. per cent.	Sodium sulphate solutions. Observed.	Calculated.	Diff. per cent.
0·050	0·1185	0·1168	−1·4	0·1191	0·1164	−2·3
0·055	0·1296	0·1277	−1·5	0·1304	0·1272	−2·5
0·060	0·1407	0·1387	−1·4	0·1416	0·1379	−2·6
0·070	0·1629	0·1604	−1·5	0·1638	0·1591	−2·9
0·080	0·1851	0·1818	−1·8	0·1856	0·1803	−2·9
0·100	0·2285	0·2241	−1·9	0·2286	0·2221	−2·9
0·200	0·4322	0·4259	−1·5	0·4330	0·4181	−3·4
0·250	0·5295	0·5250	−0·8	0·5300	0·5115	−3·5
0·300	0·6240	0·6227	−0·2	0·6252	0·6015	−3·8
0·350	0·7196	0·7200	+0·1	0·7157	0·6907	−3·5
0·400	0·8128	0·8169	+0·5	0·8100	0·7782	−3·9
0·450	0·9063	0·9131	+0·8	0·8968	0·8663	−3·4
0·500	0·9950	1·0118	+1·7	0·9875	0·9532	−3·5
0·600	1·170	1·209	+3·3	1·155	1·128	−2·3
0·700	1·341	1·406	+4·9	1·323	1·303	−1·5

The above table shows the degree of accuracy with which the depression of the freezing-point can be calculated in the case of simple solutions. If the ionisation coefficients for the mixtures are determined by Prof. MacGregor's method as closely as they are for the simple solutions by putting $a = \mu/\mu\infty$, the differences between the calculated and the observed values of the depressions in the case of the mixtures may be expected to be no greater than those of the above table.

(To be continued).

THE PHYSIOLOGICAL EFFECT OF CREATIN AND CREATININ, AND THEIR VALUE AS NUTRIENTS.*

By J. W. MALLET, M.D., LL.D.,
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(Continued from p. 56).

Experiments upon the Physiological Effects of Creatin and Creatinin.

With a view to the experiments afterwards to be made on the ingestion of creatin and creatinin, it was important to know what allowance should be made for the normal daily excretion of creatinin, and, moreover, as any increase in the elimination of urea in consequence of the ingestion of the flesh bases was one of the points to be examined, it was equally important to ascertain the normal daily excretion of urea. The figures of the first of the above tables (see *ante*) afford a basis for the establishment of average values for the normal excretion of these two substances, and show about what range of variation from the average may be looked for. In order to make this range as small as possible, and consequently to give as much value as possible to the assumption of the average for purposes of comparison, care was taken during the whole of the time in which the physiological experiments were being carried on that the conditions of food, exercise, surrounding temperature, and sleep should be as uniform as was compatible with no very inconvenient disturbance of the ordinary habits of life. Especial attention was given to the selection of a simple mixed diet of animal and vegetable materials, not at all excessive, but fully sufficient in amount, such as could be easily had with little change from day to day, for several weeks in succession. Without actually weighing the food consumed, a pretty close approach was made to uniformity in the quantity of each article, while the distribution in time of the meals was almost absolutely regular. The greatest variation probably was in the consumption of water in all forms, but this was of little importance, as all the samples of urine were weighed, not measured, and in all the experiments aliquot parts of the total daily excretion were employed. Judging by the values shown in the table (see p. 56), the daily excretion of urea appears to have been 28·922 grms. and that of creatinin 0·817 grm. (as direct results of determination by the process used).

Having in mind the general belief in the well-marked effects of Liebig's and other meat extracts upon the nervous system, it seemed needful, when the physiological experiments were undertaken, to proceed with some caution in the administration of pure creatin and creatinin, and to begin with prudently small doses and gradually increase them. It was found, however, by a number of preliminary experiments, that 1 or 2 grms. could be taken with no appreciable physiological effect; that 5 grms. gave rise to noticeable symptoms; and that 10 or even 15 grms. did not produce any very strongly marked or alarming impression. Not more than 15 grms. was used in any of the experiments, since it was desirable that the quantity given should not be in excess of that which, even in the case of the less soluble creatin, could be held in solution by the water of a probable minimum amount of urine excreted in twenty-four hours.

A quarter of an hour before the time for beginning an experiment the bladder was emptied, and just before the experiment determinations were made of the pulse rate, of the rate of breathing, of the bodily temperature (taken under the tongue), and of the reaction of the urine, test-paper being used. At a definite time, generally either 10 or 10.30 a.m., about two hours after breakfast, the dose of creatin or creatinin, previously reduced to fine powder, was swallowed with a little water.

With the larger doses there was perceived in a very short time—ten or fifteen minutes—a slight frontal headache, with a sense of constriction across the forehead, and slight ringing in the ears like that produced by quinine. These symptoms, which were of but trifling intensity, were accompanied by slight general nervous agitation, and did not last for more than an hour or two. For several hours there was a decided tendency to urinate frequently.

These general effects seemed to be the same for both the flesh bases, but were rather more marked in the case of creatin than in that of creatinin. No disturbance of digestion was perceptible from any of the doses used.

The pulse and respiration rates, the bodily temperature, and the reaction of the urine to litmus paper were observed at definite intervals. Exactly twenty-four hours after the time at which a dose had been swallowed, the bladder was again emptied; the whole of the urine for the intervening day, collected in a single vessel, was measured, weighed, and the specific gravity noted after the liquid had cooled to 15° C. The portions submitted to analysis were weighed.

The following table shows the amount of creatinin or creatin taken, the amount of urine excreted, and its specific gravity in seven experiments:—

Creatinin and Creatin taken and Urine Excreted.

Number of experiment.	Creatinin taken.	Creatin taken.	Urine excreted in twenty-four hours.	Specific gravity of urine.
	Grms.	Grms.	C.c.	
1.	5	—	1267	1·024
2.	10	—	1415	1·026
3.	15	—	1544	1·029
4.	—	3	1502	1·023
5.	—	5	1358	1·024
6.	—	10	1529	1·027
7.	—	15	1464	1·029

* *Bulletin*, No. 66, United States Department of Agriculture, Office of Experiment Stations.

Physiological Effect of Creatinin and Creatin.

	Pulse rate per minute.	Temperature. °F.	Respiration per minute.	Reaction of urine.
Experiment No. 1.—				
Just before taking creatinin	81	98·5	18	Normally acid. (*a*)
One-half hour after taking creatinin	73	98·5	18	Do.
One hour after taking creatinin	69	98·6	17	Do.
Two hours after taking creatinin	70	98·5	18	Do.
Five hours after taking creatinin	79	98 6	19	Do.
Experiment No. 2.—				
Just before taking creatinin	80	98·3	17	Decidedly acid.
One-half hour after taking creatinin	70	98·2	17	A shade less acid.
One hour after taking creatinin	(*b*) 62	97·9	15	Very faintly acid.
Two hours after taking creatinin	(*c*) 74	98·4	18	Distinctly acid, but not quite so much so as at beginning.
Five hours after taking creatinin	83	98·3	17	Acidity fully normal.
Experiment No. 3.—				
Just before taking creatinin	76	98·6	19	Normally acid.
One-half hour after taking creatinin	66	98·3	17	Acidity a shade less than normal.
One hour after taking creatinin	(*d*) 57	97·7	16	Perceptibly acid, but less so than at beginning.
Two hours after taking creatinin	(*e*) 72	98·2	18	Acidity a shade less than normal.
Five hours after taking creatinin	80	98·4	17	Acidity fully normal.
Experiment No. 4.—				
Just before taking creatin	77	98·6	16	Normally acid.
One-half hour after taking creatin	76	98·5	16	Do.
One hour after taking creatin	74	98·6	17	Do.
Two hours after taking creatin	77	98·6	18	Do.
Five hours after taking creatin	79	98·5	17	Do.
Experiment No. 5.—				
Just before taking creatin	83	98·5	19	Do.
One-half hour after taking creatin	78	98·5	18	Do.
One hour after taking creatin	74	98·3	19	Distinctly less acid than at first.
Two hours after taking creatin	77	98·5	18	Nearly of normal acidity.
Five hours after taking creatin	82	98·4	18	Normally acid.
Experiment No. 6.—				
Just before taking creatin	79	98·5	17	Rather more than normally acid.
One-half hour after taking creatin	73	98·4	17	Faintly acid.
One hour after taking creatin	69	98·5	16	Slightly alkaline.
Two hours after taking creatin	69	98·1	18	Very slightly alkaline.
Five hours after taking creatin	81	98·5	16	Acidity about normal.
Experiment No. 7.—				
Just before taking creatin	78	98·4	17	Acidity fully normal.
One-half hour after taking creatin	70	98·4	18	Acidity a little less than normal.
One hour after taking creatin	67	98·3	18	Distinctly, but not strongly alkaline.
Two hours after taking creatin	65	98·2	16	Very faintly alkaline.
Five hours after taking creatin	85	98·3	18	Practically neutral; slightly inclining to acid.

(*a*) The exact degree of acidity was not measured by means of a standard alkaline solution, but estimated by the rapidity of development and the intensity of colour produced on litmus paper of uniform character.

(*b*) With frequent and well-marked intermittence.
(*c*) With occasional slight intermittence.
(*d*) With marked intermittence.
(*e*) Intermittence scarcely perceptible.

The pulse rate, rate of respiration, body temperature, and reaction of the urine in the different tests are given in the accompanying table.

As will be seen, the most decided physiological effect produced was the retardation of the action of the heart. This was unmistakable. It seemed to be accompanied by little, if any, change in the force of impulse as felt in the radial artery; if there was any effect of this kind, it probably was a diminution of force, but there was no clear impression of such a change. The statements of others as to the flesh bases acting most perceptibly as nerve *stimulants* may perhaps be partly accounted for by smaller doses having been used by the author, and partly by evidence having been drawn from the use of meat extracts and the action of other constituents of these extracts having been confounded with the action of the pure flesh bases. The effect of creatinin as a cardiac retarder seems to be greater than that of creatin for the same dose. The latter seems also to act more slowly, this fact suggesting that its effect may be exerted, either wholly or chiefly, after it has undergone conversion into creatinin in the body, though this is hardly probable.

In the figures obtained there may possibly be traced a slight tendency to retardation of breathing and to lowering of bodily temperature, but there is no clear evidence of this.

An interesting point is the reduction of the acidity of the urine by creatin, extending—even in the case of the larger doses—to development of an alkaline reaction. Something of the same sort is observable for the larger doses of creatinin, though not to the same extent. On noticing the results of the tests made at different times after the ingestion of the flesh bases, it will be seen that the effect upon acidity, as well as that upon the heart's action, seems to have been most marked about an hour after the doses had been taken, with some tendency to longer delay in the case of creatin than in that of creatinin. In all the experiments the reaction of the mixed total excretion for twenty-four hours was acid, and apparently of about the normal intensity.

Applying to the seven specimens of urine of these experiments the method of analysis which has been described, the following results were obtained :—

Constituents of Urine excreted in Twenty-four Hours when Flesh Bases were taken.

Number of experiment.	Urea. Grms.	Creatinin. Grms.	Creatin. Grms.
1	29·096	5·386	—
2	29·457	10·097	—
3	29·558	14·816	—
4	28·973	3·170	—
5	28·735	4·742	0·014
6	30·011	8·741	0·069
7	29·714	12·699	0·177

Examining these results, there seems to be a small increase of urea—an average of 29·363 grms. per day, as against the average of 28·922 grms. obtained from the nine samples of normal urine—and perhaps a little tendency to higher figures in the experiments in which the larger doses of the flesh bases were taken. But neither of these conclusions can be drawn with any certainty, since differences between the individual results, both in the case of normal urine and also when flesh bases were taken, were greater than the difference between the two averages.

The figures for creatinin include, of course, the amount of this substance *normally* present in the urine, and therefore the amount found in each experiment must be reduced by 0·817 grm., the average value for normal creatinin as found in the nine experiments first recorded. Assuming also, on the basis of the same nine experiments, that the analytical process employed yields 95 per cent of the quantity of creatinin really present, the following are the corrected results for Experiments 1, 2, and 3, when creatinin was taken :—

Corrected Results of Tests in which Creatinin was taken.

Number of experiment.	Creatinin ingested. Grms.	Creatinin recovered. Grms.	Creatinin recovered as percentage of creatinin ingested. Per cent.
1	5	4·809	96·18
2	10	9·768	97·68
3	15	14·736	98·24

As regards creatin, it is evident at a glance that nearly all of that swallowed was converted into creatinin and eliminated in this latter form, very small amounts, however, escaping and undergoing elimination unchanged. This fact of any creatin escaping change in the rapid passage through the system of a large dose is in itself an interesting point, and such an apparent result is not probably to be explained by the supposition of change in the opposite direction having occurred during the process of analysis. It is to be noticed that the quantities of creatin found as such—in all cases small—increase with increase of the dose swallowed. In order to see how far creatin was recovered, the quantity of creatinin found has first to be reduced by the allowance for that normally present, then increased in the ratio of 95 : 100, so as to correspond with the determined degree of accuracy of the analytical method used, and then calculated to the equivalent quantity of creatin which it represents—the quantity of creatin found as such must be increased in the ratio of 86·9 : 100, so as to correspond with the determined degree of accuracy of the analytical method—and finally the creatin thus found really present as such must be added to that represented by creatinin. The corrected results for experiments 4, 5, 6, and 7 are as follows :—

Corrected Results of Tests in which Creatin was taken.

Number of experiment.	Creatin ingested. Grms.	Creatin recovered as such or represented by creatinin. Grms.	Creatin recovered as percentage of creatin ingested. Per cent.
4.. ..	3	2·872	95·73
5.. ..	5	4·806	96·12
6.. ..	10	9·749	97·49
7.. ..	15	14·703	98·02

Looking at the actual quantities of creatinin and creatin recovered, it is seen that the loss on the quantity ingested does not vary largely in the several experiments, being only somewhat greater for the larger doses than the smaller; hence the relative percentage loss is less for the former than for the latter. For both urea and creatinin it has only been possible to allow for the quantity present in the urine in its natural condition on the basis of the average of the determinations made; it must be remembered that this, therefore, conceals such differences as might have appeared if the exact normal condition of the excretion could have been ascertained on the particular day on which creatin or creatinin was administered. It is, moreover, conceivable that the normal excretion of urea or creatinin, or both, may have been altered by the very ingestion of either of the flesh bases, though this is hardly likely.

(To be continued).

NOTICES OF BOOKS.

Twenty-third Annual Report of Her Majesty's Inspectors of Explosives; being their Annual Report for the Year 1898. London: Darling and Sons, Ltd. 1899.

The Inspectors record with the deepest regret the death of their late senior colleague, Sir Vivian Dering Majendie, K.C.B. Sir Vivian had been Chief Inspector since the passing of the Act, and had been previously since 1871 in a similar position under the Gunpowder Act. It was he who was chiefly responsible for the provisions of the Explosives Act, which has now stood the test of twenty-three years working, and although many new explosives have been brought under its cognisance, and the trade has expanded in quite an unforeseen manner, the Act has proved itself equally adapted to the requirements of the present day. The vacancy in the department has been filled by the appointment of Captain Maurice Bricklade Lloyd, R.A., to be one of Her Majesty's Inspectors of Explosives.

During the past year two further modifications have taken place, the Order of the Secretary of State, No 3, having been amended in so far as it relates to the packing of small arm nitro-compounds, wet gun-cotton, and pinfire pistol cartridges, by a new Order, No. 3 (*d*). A copy of this order will be found in Appendix F (2).

The number of factories continues to increase, seven new ones having been added since 1897, while thirteen new licences are still under consideration. Two factories have become extinct during the year. We are glad to see that the number of deaths from accidents in manufacture has dropped from nine last year to two this year, both of these being caused by the same accident. The average annual number of deaths by accident during the decade is 4·8.

There have been added to the list of authorised explosives fourteen new substances which have successfully passed the necessary tests.

During the past year 184 visits have been made to factories, which now number 143; there has been no falling off in the general improvement referred to in previous reports, a very high standard of excellence has been reached, and we are glad to see it is fully maintained.

Proceedings for irregularities are now happily of rare occurrence; it is perhaps unavoidable that breaches of a minor character should be occasionally found, but as a rule they are at once rectified when attention is drawn to them. In two cases only was the institution of proceedings actually necessary.

The total number of magazines is now 387, being a decrease of three on last year, when the number stood at 390. There has been no case of proceedings being taken in respect of irregularities in a magazine, nor has there been any accident in one through fire or explosion during the year.

There has been a considerable decrease in the amount of foreign nitroglycerin compounds imported in 1898, as compared with 1897, the figures being respectively 983,600 lbs. and 1,153,550 lbs. The demand for foreign carbonite, which was so great in 1896, is now rapidly falling off, but the importation of foreign fireworks, principally from China and Japan, has increased from 234 tons to 325 tons. It is a matter for surprise that there can be a demand for such a large number of these articles.

The inspectors have no reason to modify the opinion already expressed by them, that the powers conferred upon them by Sections 55, 73, 74, and 75 are ample and satisfactory.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

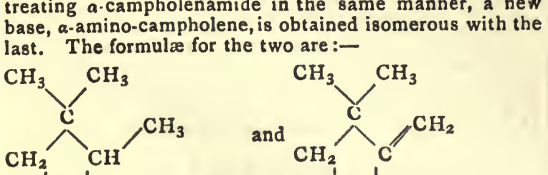
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 2, July 10, 1899.

Tetrachlor-dialcoyl-benzoylbenzoic and Dialcoyl-benzylbenzoic Acids.—A. Haller and H. Umbgrove.—A study of these acids show:—1. They are prepared under identical conditions to those which allow of the preparation of non-chlorated dialcoyl-amido-benzoyl-benzoic acids. 2. They differ from the latter in that they are not capable of being directly etherified by ordinary methods, and they do not furnish dialcoyl aniline-phthaleins when they are condensed with dialcoyl-aniline in the presence of acetic anhydride. 3. Under these conditions mixed tetrachlor-acetyl-dialcoyl-benzoyl-benzoic anhydrides are formed. 4. These anhydrides, when treated with sodium alcoholate, are transformed into ethers.

Action of Nitrogen Dioxide on the Salts of Chromium Protoxide.—G. Chesneau.—The author's investigations show that chromous salts in solution absorb nitrogen dioxide in the same way as ferrous salts, but they only give a compound containing 1 molecule of N_4O_2 for 3 molecules of the salt. This compound decomposes rapidly, especially if heated or in the presence of acids, but no gas is evolved; the action thus differing from the behaviour of the similar iron salt. The nitrogen of the dioxide is transformed into hydroxylamine or into ammonia, and the oxygen unites with the chromous salt.

Action of Phenylhydrazine on Alcoholic Bromides, Chlorides, and Iodides.—J. Allain de Canu.—The author finds, as he had predicted, that the alcoholic chlorides and bromides do not behave with phenylhydrazine in the same manner as the corresponding iodides. The higher alcoholic iodides also react in a different way from the methyl and ethyl alcoholic iodides.

Amino-campholenes.—E. E. Blaise and G. Blanc.—By treating β-campholenamide with hypobromite of potash, the authors obtain a new base, β-amino-campholene, as a colourless mobile liquid with ammoniacal smell, and boiling at 185°, its density being 0·8778 at 15°. By treating α-campholenamide in the same manner, a new base, α-amino-campholene, is obtained isomerous with the last. The formulæ for the two are:—



An Oxyptomaine. — Œchsner de Coninck. — The author prepares this oxyptomaine by the action of hydrogen peroxide on the pyridic ptomaine, $C_8H_{11}N$. It has the formula $C_8H_{11}NO$. From this substance are also prepared the bromohydrate, chloraurate, and chloromercurate.

New Method for the Acidimetric Estimation of Alcoloids.—Elie Falières.—Instead of using as an indicator litmus, or any of the ordinary indicators, to estimate the alcoloids, the author employs an ammoniacal copper solution with very good results.

Benzoyl-furfurane.—R. Marquis.—During a research on the subject of the furfuranes the author prepared benzoyl-furfurane. This ketone is easily obtained by acting on benzene with chloride of pyromucyl in the presence of aluminium chloride.

The Egols, New General Antiseptics. — E. Gautrelet.—To prepare these substances, parasulphones obtained from phenols are nitrated, and from this product the orthonitrophenolparasulphonate of mercury and potassium is prepared. The substances thus prepared are called egols—phenegol from phenol, cresegol from cresol, &c. They possess certain antiseptic properties, and they are neither volatile, inflammable, nor explosive.

Erratum.—P. 1, col. 1, *for* "William P. Cutler" *read* "William P. Cutter."

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"PATENTEE'S HANDBOOK" Post Free on application.

THE CHEMICAL NEWS.

Vol. LXXX, No. 2073.

SOLIDIFICATION OF HYDROGEN.

Professor Dewar has succeeded in solidifying hydrogen into a glassy transparent mass.

ON THE ELECTROLYSIS OF THIOSULPHATE OF AMMONIUM.

By P. PIERRON.

It has been recently proposed to introduce hyposulphites into the electrolysis of certain electro-metallurgical operations; it therefore seemed to be of importance to decide what transformations these salts may undergo under the influence of the electric current.

The experiments were carried out on aqueous solutions of thiosulphate of ammonium containing 17·5 per cent of the anhydrous salt. The action at the two poles was examined separately. The solution submitted to electrolysis was contained in a porous pot; a cylindrical platinum electrode was suspended therein; the other electrode, of lead, surrounded the pot, and was plunged into a 10 per cent solution of carbonate of ammonium; when the outer electrode is the anode there would be no inconvenience in replacing this solution by hyposulphite; when, however, it is the cathode, the hyposulphite would give sulphides by reduction, and these would carry HS– or –S– ions into the interior of the pot, and thus complicate the phenomena. The temperature was kept at about 15° by means of a cold-water jacket: platinum was first used as the cathode.

The density of the current at the cathode was from 10, 15, to 40 ampères per decimetre; the phenomenon of reduction always led to the formation of sulphide of ammonium; no other product of this action was detected, and the phenomenon was not examined any closer.

If the inner electrode is the anode the reactions are more complex; we should expect then to form some of the acids of the thionic series; the method of Fordos and Gélis has been applied to their detection. The sulphuric acid formed was estimated in the state of sulphate of barium; an iodometric titration gives the total reducing power of the sulphurous acid and of the unchanged hyposulphite: this treatment with iodine transforms the sulphites into sulphates; a fresh estimation of the sulphuric acid will thus give the proportion of sulphurous acid present; this known, it is easy to deduce from the reducing power the proportion of thiosulphuric acid present. A current of chlorine in alkaline solution transforms all the oxidised compounds of sulphur, with the exception of dithionic acid, into sulphuric acid; this is estimated, and we thus obtain the quantity of sulphur present in the three last thionic acids: finally, by evaporating to dryness, mixing the residue with three times its weight of chlorate of potash, and treating with hydrochloric acid, all the sulphur passes to the state of sulphuric acid; a final titration of this latter gives, by difference, the proportion of dithionic acid. In the experiments we made these two last determinations led to identical results. On the other hand, ammoniacal nitrate of silver is not clouded by the electrolysed ammoniacal solutions, —they hardly colour it brown,—therefore they do not contain pentathionic acid. Under these conditions we can determine the trithionic and tetrathionic acids; the neutral solution is boiled with excess of mercuric cyanide until it is no longer cloudy.

The SO_3H groups contained in the various salts of the solution are thus transformed into sulphates; the remainder of the sulphur is eliminated in the state of sulphide of mercury, or set at liberty. The sulphuric acid is estimated; from the figure found after the deduction of the quantity of sulphuric acid coming from the other acids (sulphuric, sulphurous, hyposulphurous) the quantity of sulphur contained in the thionic acids is deduced. Let P_1 be this weight of sulphur; P_2 the total thionic sulphur: if $3p_3$ is the weight of sulphur contained in the existing trithionic acid, $2p_3$ will be the weight contained in its SO_3H groupings; in the same way if $4p_4$ is the weight of the total tetrathionic sulphur, $2p_4$ will be the weight contained in the tetrathionic SO_3H groupings, from whence we obtain the equations—

$$P_1 = 2p_3 + 2p_4,\ P_2 = 3p_3 + 4p_4,$$

from which we have—

$$p_4 = \frac{P_1 - 2p_3}{2},\ \text{and}\ p_3 = 2P_1 - P_2.$$

(All these weights are expressed in sulphur). In this manner considerable quantities of tri- and tetra-thionic acids are detected.*

In 200 c.c. of the thiosulphuric solution currents of 28 ampère-hours have been passed at densities of 40, 15, and 3 ampères per square decimetre (the current used was 1·1 ampère), at a temperature of from 12 to 16°. From the commencement and during the whole time sulphur is deposited, and sulphurous anhydride given off; in an experiment at 40 ampères density this sulphur adhered strongly to the platinum, increased the resistance of contact, and caused a decided elevation of temperature of the electrode; the conditions of the experiment were thus slightly different from those of the other experiments. In all three cases the electrolyte became acid.

The method of analysis described above gave the following results:—

Density at the the anode.	40 ampères per decim.	15 ampères.	3 ampères.
S deposited ..	15·20	9 62	5·16
S sulphuric ..	7·20	5 92	5 32
S sulphurous ..	1·21	1·30	1·07
S trithionic ..	2·81	1·35	2·87
S tetrathionic .	3·99	5 70	8·71

From these figures we get the increase of the deposit of sulphur and of the quantity of sulphuric acid with the density of the current, and the simultaneous diminution of the tetrathionic acid. The proportion of sulphurous acid remains practically constant; that of trithionic acid shows a variation which is not easy to explain by reason of the complexity of the phenomena; as to its presence, it was foreseen from the work of Plessy and Rathke: the hyposulphite is here found in the presence of sulphurous acid and of acid sulphite. It is easy to understand, on the other hand, the inverse variation of the quantities of tetrathionic acid, sulphuric acid, and deposited sulphur. The tetrathionic acid evidently here results from oxidation, and not from addition, as, for example, persulphuric acid; the diminution of returns at high current densities proves this, and, further, for this addition to be possible it would be necessary for the sulphydric atoms, –S– (SO_3H), to take a prominent part in the electrolysis, and be consequently more easily dissociated than the other, which is extremely probable in the concentrated solution submitted to electrolysis. At the commencement, then, of the electrolysis some of the ions $-SO_3.S.NH_4$ are set at liberty, and split up into sulphur, sulphurous acid, and sulphate of ammonia:—

$$(2[NH_4.S.SO_3-] = SO_2 + S_2 + SO_4(NH_4)_2).$$

This latter immediately takes part in the electrolysis,

* P might be measured by determining the total alkali, after exactly neutralising the solution. In fact ammonium, NH_4, corresponds in the series to an SO_3H grouping.

forming sulphuric acid, which makes the solution acid, and oxygen, which transforms the thiosulphate into tetrathionate. If the surface of the electrode is large, at the end of a few moments the sulphate is electrolysed almost alone, being the most easily dissociated of the salts in solution, and the phenomenon of oxidation to tetrathionate goes on. If the surface is small, the electrolyte in its neighbourhood will become poor in sulphuric ions and the thiosulphate will continue to be electrolysed, giving sulphate, sulphur, and sulphurous acid; the return of tetrathionate, which is in direct relation with the quantity of sulphuric ions given off, diminishes accordingly. Besides these phenomena, an oxidation of sulphurous acid takes place, and possibly an oxidation of the thionic acids which does not allow of uniformity between the two sets of reactions: what leads to this last supposition is, that in the electrolysed solutions we do not find either pentathionic acid or sulphuretted hydrogen, which ought to be present as products of the decomposition of the hyposulphite under the slow influence of the sulphuric acid set at liberty. Small quantities of the former have been detected in the early part of the electrolysis, but they gradually disappear. It is thus evident that these bodies are destroyed during their formation by the oxidising action of the surrounding material, and the other thionic acids—although having greater resistance—should be equally destroyed. These products of the destruction of the hyposulphite are evidently oxidised at the expense of forming tetrathionate; by checking the acidity of the solution by adding ammonia during the electrolysis, we could diminish the formation of tetrathionate, and the deposit of sulphur, and the formation of sulphuric acid; experiment has confirmed this view. But the experiments made in this direction were not sufficiently exact to give very good results.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 10.

THE PLACE OF THE NEW CONSTITUENTS OF THE ATMOSPHERE IN THE PERIODIC SYSTEM.

By JAS. LEWIS HOWE.

FROM the first announcement of the discovery of argon, the interest of chemists has been engaged as to what place the element would occupy in the periodic system, and this interest has increased as the efforts of Ramsay have brought to light other closely related elements of the same nature—helium, neon, krypton, metargon, and xenon. By some it has been held that it is impossible to find a place in the system for these elements; by others, that they can be easily located. Piccini, in the *Zeitschrift für Anorganische Chemie* (xix., 295), has recently given an excellent review of the more important of these opinions. It is the purpose of this paper to consider several of the arguments on the subject.

One of the arguments which has been adduced by those who hold that the periodic system is inconsistent with the existence of these elements, is that the atomic weight of argon is apparently greater than that of potassium, and there is no place in the periodic table for an element between potassium and calcium. While there is room for it between chlorine and potassium, its atomic weight would not allow it to be placed here. This objection to the periodic table is by no means unique, for it applies equally well to cobalt and tellurium. The latest and best atomic weight determinations give cobalt a higher atomic weight than nickel, and tellurium a higher atomic weight than iodine. According to the table of Mendeleeff or of L. Meyer the reverse should be the case. The real difficulty, however, does not rest with the table. In its properties cobalt lies clearly between iron and nickel, to as great a degree as rhodium lies between ruthenium and palladium, and cobalt is undoubtedly the analogue of rhodium. Similarly, as far as investigated, the properties of tellurium seem to be between those of antimony and iodine, even as those of selenium are between those of arsenic and bromine, and, in spite of some efforts to the contrary, tellurium must be considered as the analogue of selenium, and a member of Group VI. The apparent inconsistencies in these cases rest with the facts, and the table merely reveals them. If it be true that an element lying between two others in respect of atomic weight must possess intermediate properties, then it is the atomic weight determinations which are at fault. This may indeed be the case, and, if so, errors are certainly no less probable in the case of argon than in case of cobalt, nickel, and tellurium; but if it should prove, as now seems probable, that the atomic weights in question are approximately and relatively correct, then it must follow that an element need not in every case have an atomic weight intermediate between the two elements, between which it lies in respect of properties,—that is, it may pass slightly outside of these limits. This fact would be expressed in the periodic table by an element occasionally having an atomic weight slightly greater than that of the element which follows it; but the law upon which the periodic system is based, that the properties of elements are a periodic function of their atomic weights, would still be true. We may express this idea mathematically by the equation—

$$\text{Atomic weight} = \phi(n) + \psi(m),$$

where ϕ is relatively large and simple and ψ relatively small and complex. Here, while in general the atomic weight will increase as n increases, it is possible that for certain values $\psi(m)$ may have sufficient weight to cause the atomic weight to retrograde temporarily: this would be expressed in the periodic table by certain elements having slightly higher atomic weights than the element which follows them. It is by no means impossible that the anomalous atomic weights of cobalt (or nickel) and tellurium may be accounted for in this way, and if argon should come into the same category it would throw no discredit upon the periodic system.

The question is raised by Piccini as to whether the periodic system of Mendeleeff is open to the reception of elements of which no compounds are known, and this he answers in the negative. Now if the properties of the elements are a periodic function of their atomic weights, and this is in general acknowledged by most chemists, then it must follow that the properties of argon, neon, and helium are functions of their atomic weights, or else argon, neon, and helium are not chemical elements in our ordinary sense of the term. The periodic table, as heretofore said, merely expresses in a visible, easily comprehensible way the fact of the law. It is for us, then, to consider as to whether argon, neon, and helium can find a place in this table.

Now in the table as given by Mendeleeff, as well as in that of L. Meyer, it is not clear that there is a natural place for these elements; indeed there has always been in these tables a difficulty in the relations between the short and the long periods, and especially with the eighth group, in which these new atmospheric elements fall. This Group VIII. has been a sort of catch-all into which iron, cobalt, nickel, and the platinum metals have been dumped, with little attempt at order or consideration of their properties. They are a manifest irregularity in the tables, and the tables would be as well or even better off did these metals not exist. As a matter of fact, however, this Group VIII. plays a very important part if the table is arranged on an upright cylinder, in the form adopted by L. Meyer in the third edition of his "Moderne Theorie der Chemie." Here it is clearly seen that Group VIII. is as much a transition group, for three periods, from Group VII. to Group I., as Group IV. is a transition group from III. to V. The relations of the new elements is most clearly seen by means of the subjoined table, which is practically that of Venable. While Venable's table was first proposed merely as a convenient form for teaching,

M_2O	MO	M_2O_3	MO_2 H_4M	M_2O_5 H_3M	MO_3 H_2M	M_2O_7 HM	
H (?)							He
Li	Gl	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni
Cu	Zn	Ga	Ge	As	Se	Br	? [82] ? [84]
Rb	Sr	Y	Zr	Cb	Mo	—	Ru Rh Pd
Ag	Cd	In	Sn	Sb	Te	I	
Cs	Ba	La	Ce	*	*	*	* * *
†	†	†	†	†	†	†	
*	*	*	*	Ta	W	*	Os Ir Pt
Au	Hg	Tl	Pb	Bi	†	†	
*	*	*	Th	*	U		
+ Series.	− Series.	+	−	+	−	+	−

* Possible + series elements. † Possible − series elements. — Ekamanganese.

it deserves far wider recognition, as it brings out the natural relations of the elements in many respects more clearly than any other form of table, and at the same time avoids certain difficulties which appear in other tables, especially that regarding the short and long periods. The table here given differs from that of Venable chiefly in leaving places for possible elements with atomic weights greater than 140, and in placing helium, neon, and argon in what appears to be their natural position.

Here the three new elements appear clearly as transition elements between the halogens and the alkalis, except that there is no halogen of lower weight than fluorine. Is this position justifiable? The arguments in its favour are not new, but may be here repeated for emphasis.

a. Elements with no chemical affinity would be a natural transition from the strongly negative halogens to the strongly positive alkali metals.

b. The valence toward hydrogen being in Group IV. four, in Group V. three, in Group VI. two, and Group VII. one, would naturally in Group VIII. be zero, which expresses the fact that these elements form no compound with hydrogen.

c. Towards oxygen and other negative elements we have, in Groups IV., III., II., I., respectively a valence of four, three, two, one; in Group VIII. we should then expect a valence of zero, and this is expressed by the fact that the new elements form no compounds with negative elements, as far as experiment has yet shown.

It is not inconceivable that these elements might have even a valence of eight toward oxygen, following the analogy of the halogens with a valence of seven; but valence is greatly modified by electro-chemical character, as is shown by the fact that, while from its position a compound Fl_2O_7 might be expected, fluorine—owing to its

electro-chemical character—forms no compound at all with oxygen.

The question, however, arises at once regarding the nine metals of Group VIII., if the above arrangement holds good. To explain this we must consider Venable's table. To the elements of the first period (lithium—fluorine) he gives the name of *group* or *bridge elements*; to those of the second period (sodium—chlorine) *type elements*, as *they*, rather than the *group elements*, foreshadow the character of the succeeding elements of the respective groups. After the type element each group divides into two series, a positive and a negative, as shown in the table. Now the Group VIII. metals mark the transition from the positive series of the Group VII. to the negative series of Group I. Now since the electro-chemical character of manganese differs little from that of copper, and that of eka-manganese would differ little from that of silver, we have in these cases a gradual transition through iron, cobalt, and nickel, respectively ruthenium, rhodium, and palladium. Manganese and copper both form compounds with oxygen and chlorine in which the positive elements are bivalent, and we find the same true of iron, cobalt, and nickel. Manganese acts also with higher valences toward oxygen, and we find the same true with iron, cobalt, and nickel, iron approaching manganese most closely in this respect, and cobalt next. An analogous line of argument applies to the ruthenium group and to the osmium group. Argon, on the other hand, is a transition element from the type element (negative) chlorine of the most strongly negative Group VII. to the positive series of the most strongly positive Group I.

There seems, however, at first sight, to be a decided inconsistency in placing these inert elements—helium, neon, and argon—in the same group with iron, cobalt, nickel, and the platinum metals. From its position argon would seem to be the *type element*, but the metals of this group in no way resemble it. We notice from the table that in Group I. the elements of the positive series very closely resemble the type element, sodium. In Group II. the positive series elements resemble magnesium, but not quite so closely. This resemblance of the elements of the positive series to the type element decreases continuously until in Group VII., the least positive group, the only element of the positive series, manganese, bears very little resemblance to the type element, chlorine. In Group VIII. it is, then, not unexpected that this resemblance wholly disappears, and we find no similarity between iron, cobalt, nickel, and the platinum metals on the one hand, and argon on the other.

Proceeding in the reverse direction, the change differs only in degree. In Group VII., the most negative group, the elements of the negative series, bromine and iodine, very closely resemble the type element chlorine, and this resemblance decreases continuously until in Group I., the least negative group, the elements of the negative series differ very decidedly from the type element sodium. In Group VIII. all resemblance disappears. There is therefore nothing inconsistent with this location of the new elements in Group VIII. of the periodic table.

One other point tells strongly in favour of the view that helium, neon, and argon are true elements, which is implicitly brought out by Ramsay in his recent address before the Deutscher Chemischen Gesellschaft. The first natural relation which was discovered between the chemical elements was Döbereiner's *law of triads*, and it was this idea which led Ramsay to that wonderfully painstaking and happily successful search for neon. Like so many other groups of elements, the three elements helium, neon, and argon agree with the relations pointed out so long ago by Döbereiner, and this indicates that the elemental nature of these gases is not different from that of the other elements.

A few words may be said in conclusion regarding the other gases which Ramsay met in his search for neon, *i.e.*, krypton, metargon, and xenon. Too little is yet known of them to render it possible to locate them in the periodic table; but it can readily be seen that there is sufficient space for them in the Group VIII., should their atomic weights so indicate. Whether Group VIII. itself should not be split up into three distinct groups is an open question Certain it is that in many respects the three triads—iron ruthenium, and osmium; cobalt, rhodium, and iridium; nickel, palladium, and platinum—differ from each other in no small degree, perhaps sufficiently to deserve to be placed in three distinct groups. If this be the case, it may be that there would be a group element and a type element for each group, as well as elements corresponding to the copper-bromine period, and perhaps to the higher missing periods. Or, on the other hand, two transition elements might occur between bromine and rubidium, of atomic weight of about 82 and 84 respectively, taking their place between the iron, cobalt, and nickel triads; corresponding to these would be two type elements for Group VIII., of which metargon might be one. This is of course mere speculation, but it serves to show that there is room not only for helium, neon, and argon in this Group VIII., but also for other elements of similar properties, and this without doing violence to the periodic law, which must be considered as the greatest generalisation of modern chemistry.

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ON A TEST, BY THE FREEZING-POINT METHOD, OF THE IONISATION COEFFICIENTS DETERMINED BY THE CONDUCTIVITY METHOD, FOR SOLUTIONS CONTAINING POTASSIUM AND SODIUM SULPHATES.*

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(Concluded from p. 69).

Depression of the Freezing-point by the Mixtures.

THE accompanying table contains the observed and calculated values of the depression of the freezing-point in the case of the mixtures examined. The observations were made in the manner described above. The calculations were made by the following formula, for which I am indebted to Professor MacGregor:—

$$\Delta = 1{\cdot}86\ (1+\alpha_1+\alpha_2)\ N/2;$$

where α_1 and α_2 are the ionisation coefficients of the respective electrolytes in the mixture and N the number of grm.-equivalents per litre in the solutions mixed, which were in all cases equimolecular. This expression may be readily obtained as follows:—In each litre of the mixture there will be N/4 grm.-molecules of each electrolyte. There will therefore be $(1-\alpha_1)\ N/4$ and $(1-\alpha_2)\ N/4$ undissociated grm.-molecules of the respective electrolytes, and, if we assume the ionisation in each case to be complete, $3\ \alpha_1\ N/4$ and $3\ \alpha_2\ N/4$ free grm.-ions. Hence the total number of undissociated grm.-molecules and free grm.-ions will be $(1+\alpha_1+\alpha_2)\ N/2$, and the expression for the depression will consequently be as above.

The first column of Table V. gives the concentration of the solutions mixed, in grm.-equivalents of anhydrous salt per litre at 18° C. The fifth and sixth columns give the ionisation coefficients of the respective electrolytes in the mixture at 0° C. as determined by Prof. MacGregor's method. The second, third, and fourth give the quantities obtained directly by this method, viz., the common concentration of ions, and the dilutions of the respective electrolytes in the mixture. (By the concentration of ions

* From the *Transactions of the Nova Scotian Institute of Science*, vol. x., Session 1898-99.

TABLE V.

Concentration of constituent solutions at 18° C. (grm.-equiv. per litre).	Concentration of ions in mixture at 0° C.	Dilution in mixture at 0° C.		Ionisation coefficients in mixture at 0° C.		Depression of freezing-point.		
		$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.	K_2SO_4.	Na_2SO_4.	Observed.	Calculated.	Diff. per cent.
0·050	0·0377	20·04	19 96	0·7555	0·7525	0·1187	0 1166	−1·8
0·055	0·0410	18·22	18·14	0·7470	0·7437	0·1299	0·1274	−1 9
0·060	0·0443	16·72	16 60	0·7407	0·7354	0·1411	0·1382	−2·1
0·070	0·0509	14·40	14·18	0·7330	0·7218	0·1634	0·1598	−2·2
0·080	0·0574	12·60	12 40	0 7232	0·7118	0·1854	0 18·2	−2 3
0·100	0·0698	10·18	9·92	0·7106	0 6924	0·2284	0 2235	−2·1
0·150	0·0998	6·73	6 6	0 6717	0·6587	0·3327	0 3250	−2 3
0·200	0·1266	5·10	4·90	0·6457	0·6203	0·4324	0 4215	−2·5
0·250	0·1528	4·10	3·90	0 6265	0·5959	0·5295	0 5166	−2 4
0·300	0·1784	3·46	3·21	0 6173	0·5727	0·6246	0·6110	−2·2
0·400	0·228	2·63	2·37	0·5996	0·54 4	0·8096	0·7961	−1·7
0·500	0·227	2·12	1·88	0·5872	0 52 8	0·9885	0·9802	−0·8
0·600	0·327	1·79	1·54	0 5853	0·5036	1·1604	1 1657	+0·5
0·700	0·376	1 54	1 31	0·5790	0·4926	1·3300	1·3489	+1·4

in the mixture is meant the number of dissociated grm.-equivalents of either electrolyte in any volume of the mixture divided by the volume of that portion of the mixture which may be regarded as occupied by it. The dilutions of the electrolytes in the mixture are the volumes of such portions divided by the number of grm.-equivalents of the electrolytes they contain. The product of these two quantities for each electrolyte gives the ionisation coefficient of such electrolyte in the mixture). The data of the other columns are sufficiently specified by the headings.

If we compare the percentage differences of Table V. with the corresponding differences in the case of the constituent simple solutions (Table IV.), it will be seen that the former are in general equal to the arithmetric means of the latter. Hence the depressions of the freezing-point of the mixtures have been calculated with the same degree of accuracy as those of the simple solutions.

The test which has thus been applied to Professor MacGregor's method of determining the ionisation coefficients in a solution containing two electrolytes with a common ion, and which the method has completely satisfied, is, however, not a severe one. It was intended, after the experiments on equimolecular solutions, to take up mixtures of solutions of different concentrations with respect to the two electrolytes. Unfortunately, I was prevented from doing so by lack of time.

In conclusion, I wish to express my thanks to Prof. MacGregor for valuable suggestions kindly given.

THE PHYSIOLOGICAL EFFECT OF CREATIN AND CREATININ, AND THEIR VALUE AS NUTRIENTS.*

By J. W. MALLET, M.D., LL.D.,
Professor of Chemistry in the Univers ty of Virginia.

(Concluded from p. 71).

Conclusions.

THE main conclusion to be drawn is manifestly this:—That by far the larger part of the flesh bases ingested, if not absolutely the whole, does not undergo metabolism with the production of urea or anything else, but, on the contrary, is eliminated by way of the kidneys. In the case of creatinin it is excreted unchanged, while creatin is changed wholly or very largely into creatinin.

This elimination in the urine of the flesh bases is reflected in the figures giving the specific gravity of the excretion. Two experiments only were made with a view to ascertaining whether any of the creatin or creatinin taken in heavy doses could be recovered from the aqueous extract of the fæces, it seeming possible that the comparatively slight solubility of creatin in particular might lead to some of it escaping absorption along the course of the intestinal canal. In these two cases the results were altogether negative.

The fact of the quantitative recovery of creatin and creatinin from the urine evidently accords fully with the generally accepted belief that these substances cannot serve to build up proteids, and therefore are not to be classed among tissue-forming food materials.

On the whole, this investigation is unfavourable to the idea of the creatin of living muscle being the main antecedent of urea in nitrogenous metabolism. It is, of course, conceivable that the creatin of the living muscles may be *slowly* metabolised with production of urea, and that, as Voit has remarked, the cause of the ingested flesh bases appearing in large amount in the urine, instead of undergoing conversion into urea, may be that time enough has not been allowed for metabolism, but this is rendered very improbable by the large quantity of urea given off daily. It can hardly be admitted that such slow and difficult formation of urea from creatin can possibly represent the regular course of change by which the bulk of the urea is produced. It must be remembered, of course, that creatin swallowed, as in the above experiments, and getting into the blood by absorption from the alimentary canal, does not follow exactly the same course and is not placed under exactly the same conditions as that found in and derived from the living muscles. However, it is not easy to imagine such a difference in the fate of the same substance from these two sources, once having become a constituent of the blood, as would account for its being in the one case metabolised and in the other eliminated unchanged or merely converted into its anhydride, creatinin.

However this may be, and admitting that it is still an unsolved problem, what nitrogenous substance or substances may properly be regarded as intermediate between muscle proteids and urea, it may fairly be regarded as established for nutrition investigations that the so-called flesh bases, creatin and creatinin, occurring in food may be entirely disregarded as sources of energy, being excreted practically without having undergone change.

This conclusion seems to be deserving of attention—on the one hand, by the analyst of food materials, and, on the other by the physician who prescribes and the consumer who makes use of the ordinary meat extracts.

In the discussion of the results of analyses of meat and forms of food prepared from it, such as soups and the like, it is evidently wrong and misleading to confound together, under the head of protein or proteid materials, the proteids proper, capable of building up the nitrogenous tissues of the living body and of furnishing muscular energy and heat by oxidation, and these so-called flesh

* *Bulletin*, No. 66, United States Department of Agriculture, Office of Experiment Stations.

bases, which, taken in along with food, are not available for either of these important purposes. This error is the more serious that creatin and creatinin, containing so large a percentage of nitrogen as they do, appear to represent and are counted as representing much more than their own weight of nutrient material, whereas they should be excluded altogether in food analyses from the nutrient material really present.

As regards the practical use of meat extracts, those forms of such preparations from which the proteids and peptones have been removed, may well be considered as destitute of nutritive value, and those in which, along with some proteid material, the flesh bases occur in large quantity may be considered as deriving no nutritive value from this latter source.

Even if viewed in the light of nerve stimulants only, and thus to be classed with tea and coffee as adjuncts to food rather than as true food itself, meat extracts, so far as the flesh bases creatin and creatinin are concerned, are shown by this investigation to be very much less active in their effects upon the nervous system than they have been commonly reputed. The potassium salts present in large quantity in meat extracts, are by no means to be overlooked as influencing such effects as are produced upon the living organism, and it may be that some of the minor organic constituents are relatively more potent than creatin and creatinin, but aside from such real proteid or peptonic material as is in some cases present, the meat extract preparations may fairly be relegated on the whole to the class of condiments or flavouring matters rather than to that of foods or medicines.

Suggestions for Further Investigations.

It is desirable that the following points suggested by this investigation should, if possible, be examined. To this end it might be desirable—

1. By experiments, with other persons as subjects, to ascertain the influence, if any, of age, sex, &c., upon the behaviour of the flesh bases in the living organism.

2. To try the effect of a given amount of creatin or creatinin, administered at once as a single dose, as compared with the same quantity divided into several parts, administered as separate doses, and distributed over several hours with but short intervals.

3. To try to recover creatin or creatinin (administered by the mouth) from the blood of one of the lower animals killed or heavily bled soon after receiving a large dose of the flesh base. This would involve the interesting question whether creatinin can undergo conversion into creatin in the alkaline blood and such reaction be afterwards reversed in connection with elimination by the kidneys.

4. To examine, not the whole urinary excretion of twenty-four hours, but several samples of urine taken at short successive intervals for two or three hours after the ingestion, by swallowing, of a large dose of creatin or creatinin, so as to get a more definite idea of the rapidity with which elimination takes place, to obtain further evidence ae to creatin being capable of passing through the renal filter without conversion into creatinin, and to see whether the reverse change can occur.

5. To examine more fully the observed reversal of the normal acid reaction of the urine after ingestion of a large amount of creatin.

Metallic Sulphantimonites. — M. Pouget. — The action of metallic salts on a solution of sulphantimonite of potassium gives, by double decomposition:—1. A trimetallic sulphantimonite, SbS_3M_3. 2. A double sulphantimonite, SbS_3M_2K. (In no case was the author able to prepare the monometallic salt, SbS_3MK_2). The double decomposition is sometimes accompanied by a reduction. Solutions of orthosulphantimonites of sodium and lithium give similar results.—*Comptes Rendus*, cxxix., No. 2.

THE TITRATION OF OXALIC ACID BY POTASSIUM PERMANGATATE IN PRESENCE OF HYDROCHLORIC ACID.*

By F. A. GOOCH and C. A. PETERS.

Löwenthal and Lenssen (*Zeit. Anal. Chem.*, i., 329) were the first to show that the titration of a ferrous salt by potassium permanganate in the presence of hydrochloric acid, according to the process of Margueritte (*Ann. de Chim. et de Phys.*, [3], xviii., 244) is vitiated by the evolution of chlorine outside the main reaction, and to point out that a remedy for the difficulty is to be found in the titration of the ferrous salt in divided portions, other equal volumes of the ferrous solution being added to the liquid in which the first titration is accomplished until the amount of iron indicated by successive titrations becomes constant.

Kessler (*Ann. d. Phys. u. Chem.*, cxviii., 48; cxix., 225) showed the restraining influence of certain sulphates, of manganous sulphate in particular, upon the irregular and undesirable interaction of the permanganate and hydrochloric acid; and Zimmermann (*Ann. d. Chem.*, ccxiii., 302), in apparent ignorance of Kessler's forgotten proposal, advocated the introduction of a manganous salt, best the sulphate, into the ferrous salt to be determined, thus accomplishing the purpose of the empirical procedure of Löwenthal and Lenssen.

The tendency toward evolution of chlorine in the oxidation of a ferrous salt by permanganate, as compared with the absence of such tendency in the similar oxidation of oxalic acid, in presence of hydrochloric acid, was explained by Zimmermann on the hypothesis that an oxide of iron higher than ferric oxide is formed as an intermediate product, and that this unstable oxide is sufficiently active to break up hydrochloric acid as well as to oxidise more of the ferrous salt. Quite recently, Wagner ("Maasanalytische Studien, Habilitationsschrift," Leipzic, 1898) finds explanation of the sensitiveness of the hydrochloric acid solution of the ferrous salt in the probable formation of chlor-ferrous acid (analogous to chlorplatinic and chlor-auric acids), which suffers oxidation more readily than hydrochloric acid under the action of the permanganate. The protective influence of the manganous salt turns apparently, as Zimmermann suggested, upon the initiation of Guyard's reaction, according to which the permanganate and manganous salt interact to form a higher oxide of manganese of a constitution approaching the dioxide more or less closely—this oxide being capable of oxidising the ferrous salt, but slow to act upon the hydrochloric acid or the chlor-ferrous acid of Wagner. According to Volhard (*Ann. d. Chem.*, 1879, cxcviii., 318), the reaction of Guyard is favoured and hastened by heat and concentration of the solution, while it is delayed by acidity and dilution; but even in solutions containing very little manganous salt and a considerable quantity of free acid the faint rose colour developed by the careful addition of permanganate ultimately vanishes until every trace of the manganous salt is precipitated. When a considerable amount of the salt is present, interaction follows immediately the introduction of the permanganate. Zimmermann advocates the use of 4 grms. of manganous sulphate uniformly in titrations of a ferrous salt by permanganate—a procedure to which Wagner gives acquiescence, though pointing out that a ninth of that amount is all that he finds to be necessary. The excess of the manganous salt can do no harm so long as the higher oxide, the product of interaction of the manganous salt and the permanganate, is immediately reduced by even traces of a ferrous salt, and this appears to be the case at least within the limits proposed by Zimmermann and Wagner. Thus we

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. vii., June, 1899.

TABLE I.

Total volume at beginning of titration. C.m.³.	HCl. Sp. gr. 1·09. C.m.³.	$FeCl_2$ C.m.³.	$KMnO_4$. 1/10 N. C.m.³.	$MnSO_4.5H_2O$. Grms.	$MnCl_2.4H_2O$. Grms.
135	10	25	21·70	1	—
135	10	25	21·70	3	—
135	10	25	21·70	5	—
135	10	25	21·75	7	—
135	10	25	21·75	10	—
145	20	25	21·75	10	—
175	50	25	21·75	10	—
135	10	25	21·70	—	1
135	10	25	21·70	—	2
145	20	25	21·70	—	2
155	30	25	21·75	—	3
165	40	25	21·70	—	4

TABLE II.

(Temperature at beginning about 80° C.).

Approximate volume at beginning of titration. C.m.³.	H_2SO_4. 1 : 1. C.m.³.	HCl. Sp. gr. 1·09. C.m.³.	Ammonium oxalate. 1/10 N. C.m.³.	$KMnO_4$. C.m.³.	Variation from mean of A taken as standard. C.m.³.
			A		
200	5	—	50	47·50	0·00
200	5	—	50	47·50	0·00
200	10	—	50	47·50	0·00
200	10	—	50	47·50	0·00
200	25	—	50	47·50	0·00
200	25	—	50	47·50	0·00
			B		
150	10	2·5	25	23·80	+0·05
150	10	2·5	25	23·90	+0·15
150	10	5·0	25	23·90	+0·15
150	10	10·0	25	24·00	+0·25
500	5	—	25	23·80	+0·05
500	10	10·0	25	24·00	+0·25
500	10	10·0	25	24·10	+0·35

TABLE III.

(Temperature at beginning about 80° C.).

Volume at beginning. C.m.³.	H_2SO_4. 1 : 1. C.m.³.	Ammonium oxalate. 1/10 *n*. C.m.³.	$MnSO_4.5H_2O$. Grms.	$KMnO_4$. C.m.³.	Variation from standard.
130	5	25	—	23·75	0·00
130	5	25	0·0008	23·75	0·00
130	5	25	0·0032	23·75	0·00
130	5	25	0·0160	23·75	0·00
130	5	25	1	23·70	−0·05
130	5	25	2	23·75	0·00
130	5	25	2·5	23·60	−0·15
130	5	25	3·0	23·40	−0·25
130	5	25	4·0	23·60	−0·15
500	5	25	—	23·80	+0·05
500	5	25	0·0008	23·80	+0·05
500	5	25	0·0032	23·80	+0·05
500	5	25	1	23·70	−0·05
500	5	25	2	23·40	−0·35
500	5	25	3	23·50	−0·25
500	5	25	4	23·30	−0·45
130	10	25	1	23·80	+0·05
130	10	25	2	23·75	0·00
130	10	25	3	23·65	−0·10
130	10	25	4	23·50	−0·25
130	15	25	2	23·75	0·00
130	15	25	4	23·70	−0·05
130	15	25	5	23·50	−0·25
130	30	25	2	23·75	0·00
130	30	25	4	23·70	−0·05
130	30	25	5	23·75	0·00

find, as shown in results of Table I., that so much as 5 grms. of the sulphate may be present in 135 c.m.³ of the liquid containing about 5 c.m.³ of hydrochloric acid of full strength, without interfering with the regularity of the titration; and the effect is trivial even when the amount of manganous sulphate reaches 10 grms. We find, also, practical regularity of working when manganous chloride is substituted for the sulphate, and in this

respect our results accord with those of Zimmermann and differ from those of Wagner (*loc. cit.*, p. 104).

In all cases, however, in which the larger amounts of manganous salt are present, the end-reaction is marked by the advent of a brownish red precipitate rather than the clear pink of the soluble permanganate, and it is obvious that in case the solutions to be oxidised were not active enough to act with rapidity upon the product of the Guyard reaction, difficulty might follow the failure to adjust the conditions more particularly.

It has been stated by Fleischer ("Volumetric Analysis," trans. by Muir, p. 71) and Zimmermann (*loc. cit.*) that hydrochloric acid interferes in no way with the titration of oxalic acid by potassium permanganate. This statement, however, is not in accord with our experience; for we find that in such titrations there is a small though real waste of permanganate proportionate to the amount of hydrochloric acid present. This fact is brought out clearly in the comparison of experiments of Section A (Table II.), in which no hydrochloric acid was present, with experiments B, in which hydrochloric acid was present.

From these results it is evident that, though the error introduced by the presence of the hydrochloric acid during the action of the permanganate upon the oxalic acid is small, it is plainly appreciable. The questions arise, therefore, first, as to whether the secondary action of the permanganate upon the hydrochloric acid may be prevented by the presence of a suitable amount of a manganous salt: and, secondly, as to whether in this event the reducing agent—the oxalic acid—is sufficiently active, like the ferrous salt, to prevent the premature establishment of an end colour due to the Guyard reaction. The latter question must naturally be settled before the former can be taken up. In Table III. are recorded the effects of varying amounts of manganous salt in presence of different amounts of sulphuric acid in the reaction of permanganate upon oxalic acid.

From the results given it is evident that the persistence of the Guyard reaction is liable to interfere with the end-reaction of oxidation of oxalic acid unless an adjustment is made between the quantity of the manganous salt, the amount of acid, and the dilution. In hot solutions of a total volume of 130 c.m.^{3} at the beginning, no more than 2 grms. of the manganous sulphate should accompany 5 to 10 c.m.^{3} of the 1 : 1 sulphuric acid; when the total volume at the beginning reaches 500 c.m.^{3}, no more than a single grm. of the salt should be present with 5 c.m.^{3} of the 1 : 1 sulphuric acid. The amount of manganous salt may, however, be increased considerably if the quantity of acid is increased.

(To be continued).

Researches on Argon and its Combinations.—M. Berthelot. — The author, having obtained from Prof. Ramsay a large quantity of argon, repeated his former experiments on the reaction between argon and certain metallic compounds. Negative results were obtained when argon was mixed with ethylene, glycollic ether, aldehyde, acetone, amylene petroleum ether, propionitrile, allyl sulphocyanide, or amylamine, and the mixture subjected for some time to the action of the silent electric discharge. In all these cases the original volume of argon was recovered unchanged. In the case of mixtures of benzene, toluene, cymol, turpentine, anisol, phenol-benzaldehyde, aniline, phenyl sulphocyanide, or benzonitrile with argon, being subjected to the same treatment, argon was absorbed to the extent of 1 to 6 per cent of the total volume. At the same time a greenish fluorescence appeared, giving a characteristic spectrum. — *Comptes Rendus*, cxxix., No. 2.

ON THE

CLAIMS OF DAVYUM TO RECOGNITION AS A CHEMICAL ELEMENT.*

By J. W. MALLET.

In the year 1877 the Russian chemist, Sergius Kern, announced (*Compt. Rend.*, lxxxv., 72; CHEM. NEWS, xxxvi., 4, 114, 155, 164, and xxxvii., 65) that in treating native platinum ore he had detected a new metal of the platinum group, which he proposed to name in honour of Sir Humphry Davy. A brief description was given of the process by which the separation of the metal was effected, and some of its reactions were described. The metal itself was said to be silvery in appearance, fusible with difficulty by means of the oxy-hydrogen blowpipe, hard, and to some extent ductile, of sp. gr. 9·385 at 25° C. Only 0·27 grm. was obtained from 600 grms. of the platinum ore, = 0·045 per cent., and in subsequent papers the author spoke of it as still more sparingly obtainable, saying that most of the platinum ore used contained but 0·0008—0·001 per cent, that only a few samples gave as much as 0·035—0·045 per cent, and that the whole quantity of davyum obtained was "so small that no serious experiments could be made." The only report by another chemist on the existence of this claimant for distinct elementary character seems to be a very short paragraph in Valentin's "Course of Qualitative Chemical Analysis" (6th edition, 1884), in which the editor, Dr. W. R. Hodgkinson, says that he has obtained a small quantity of the new metal from native platinum, and has found that "it decomposes water in presence of H_2SO_4, the oxide formed scarcely dissolving in the acid"—a very remarkable statement in regard to a metal of the platinum group.

Most compilers of chemical handbooks have either ignored davyum altogether, or have relegated it to mere mention among the sundry "supposed elements," of which the list is not a short one. It is desirable that this list be as far as possible expurgated, and any experiments tending to establish or overthrow belief in the existence of a supposed element have some interest.

The point which seems to make it particularly interesting to decide whether there is such a metal as davyum or not, is the statement by Kern that the atomic mass, as determined in preliminary experiments by Alexejeff, must be near to 154. This would suggest the possible existence in the "periodic" classification of the elements of a hitherto unrecognised element, or more probably a triad of elements, analogous to the triads—ruthenium, rhodium, palladium, and osmium, iridium, platinum—and having an average atomic mass about half way between these two sets of three. Thus we should have:—

Ruthenium	100·91		?	Osmium	189·55
Rhodium..	102·23		Davyum 154?	Iridium..	191·66
Palladium	105·56		?	Platinum	193·41

It is noteworthy that in Mendeleeff's arrangement of the elements in groups and series, we have representatives of the eighth group in the fourth, sixth, and tenth series, but none in the eighth series, a place which would be taken by elements with atomic masses approximately equal to that attributed to davyum. So that, if the existence of davyum were established, it would render probable the subsequent discovery of two more metals analogous to it.

As the best means of securing a favourable chance for investigating the existence or non-existence of the supposed element, I wrote two or three years ago to Mr. George Matthey, F.R.S., of London, knowing the generous readiness to aid scientific research which he and the eminent firm of platinum manufacturers to which he belongs have always shown. I stated to him the object which I had in view, and asked whether he would be willing to let me have the use of such residues from the working on

* From the *American Chemical Journal*, Vol. xx., No. 9.

the large scale of native platinum as might most probably yield davyum, any of the already known platinum metals separated therefrom to be returned. His reply was most cordial, and he obligingly offered the free use of such residues as I should designate. The feature in Kern's description of his new element which seemed to offer the best starting-point was the very slight solubility of the double chloride of davyum and sodium, and I suggested to Mr. Matthey that if, without too much trouble or disturbance of the usual course of working native platinum, the solution in *aqua regia* of the crude material, cleared by decantation from the insoluble osmiridium, &c., and by precipitation with ammonium chloride from the bulk of the platinum, could be evaporated to dryness with a large excess of common salt, and the residue re-dissolved in a minimum of water, any sparingly soluble material left behind by this second solution might be expected to contain the element sought for, and should be collected and sent to me. He very kindly promised that this should be done, but it was not feasible to take up the matter for some months. Meantime Mr. Matthey informed me that in the precipitation of platinum from certain liquors, a solution of ammonium chloride saturated with sodium chloride was often used, and that by evaporation of the clear solution (after precipitation) coloured crystals of impure sodium chloride with a little ammonium chloride were produced; this crude salt he thought might be worth examination, and he offered to send me some of it. In due time I received about a pound of this rose-coloured common salt, and later a specimen of the residue obtained by treating a lot of native platinum as I had suggested—35 kilogrms.* of Russian platinum mineral had yielded 13 grms. of residue, and of this about half was sent me. Mr. Matthey stated in a letter accompanying the sample of residue that the process had been unusually tedious, in consequence of the fact that in the second crystallisation, when the liquor was saturated with sodium chloride, such a dense mass of crystals formed to be re-dissolved only by the cautious use of cold water, as to require a very long time for solution and settlement. The two materials for examination, therefore, were this residue, obtained in accordance with my suggestion as to treatment of the complex solution of the metals from native platinum with sodium chloride, and the rose-coloured crystals of impure common salt from the regular course of procedure offered me by Mr. Matthey.

It was at once apparent on inspection of the former of these—the residue from special treatment—that it was not likely to be the sodio-chloride of any metal. It was an exceedingly fine grey powder, with minute glistening specks, and proved to be insoluble, not only in water, but in ordinary acids, It was hard enough to readily scratch glass, and even made some minute scratches upon rock crystal, when rubbed on by means of cork or wood. Seen under the microscope it exhibited a multitude of transparent colourless granules, with a smaller proportion of steel-grey or black, opaque and brilliantly lustrous little crystals, most of which were hexagonal plates with (plane) angles of 120°, and a few angles which measured a little more than 127°. Many fragmentary crystals were visible, and a few had the appearance of elongated blades. Many of the perfect crystals, while very minute, were beautifully sharp and well defined. Treatment with gently heated hydrofluoric acid drove off much silicon fluoride, and heating of what remained with concentrated sulphuric acid rendered soluble a small amount of zirconium sulphate with a trace of iron. The residue from the action of both acids was mixed with sodium chloride in fine powder, and at a dull red heat exposed to the action of moist chlorine gas; this, Wöhler's process for decomposing osmiridium, proved easily effective in consequence of the fine state of division of the material, and yielded osmium volatilised mainly as the tetroxide, and iridium with a little rhodium left behind as sodio-chloride. It was evident that the material sent from London consisted merely of such part of the insoluble matter of the native platinum as *aqua regia* had left behind in so extremely fine a state of subdivision that it had remained suspended through the no doubt careful settling and decantation to which the platinum solution had been subjected. It is interesting to find so very dense a substance as osmiridium thus long held in suspension. After deduction of rather more than 1 per cent of hygroscopic moisture, the composition of this residue was approximately—

Quartz ..	40·8			
Zircon ..	15·4			
Osmiridium	43·8 = about	Iridium	30·2	(decomposition by chlorine not quite complete).
		Rhodium	1·4	
		Osmium	12·2	
	100·0			

(To be continued).

* This quantity, at the lowest proportion reported by Kern, viz., 0·0008 per cent, should have contained 0·280 grm. of metallic davyum, or, at the highest proportion reported, 0·045 per cent, 15·750 grms.

OBITUARY.

SIR EDWARD FRANKLAND.

It is with great regret that we announce the death of Sir Edward Frankland, which took place on Wednesday, the 9th inst., in Norway, where he had gone to indulge in his favourite pastime of salmon fishing. This country thus loses one of her most distinguished chemists, a man whose range was of extraordinary width and variety, whose brilliance as an experimentalist was unrivalled, and who made notable additions to our knowledge in almost every one of the numerous branches of chemical science to which he devoted his attention.

Born at Churchtown, near Lancaster, in 1825, he was educated at Lancaster Grammar School, and afterwards studied chemistry at the Museum of Practical Geology and in the laboratories of Liebig and Bunsen, at Giessen and Marburg. He had barely attained his majority when he began to engage in original work in pure chemistry, and even his earliest researches had an important influence on the development of chemical theory. Undertaken in conjunction with Kolbe and prosecuted in the laboratories of Playfair and Bunsen, these were at first analytical in character, their aim being the isolation and identification of the proximate radicals composing certain organic bodies. Soon, however, he began to turn his attention to synthetical problems, to the artificial building up of organic bodies, and here his efforts were rewarded by the important discovery of the organo-metallic compounds resulting from the direct union of a positive organic radical with a metal. It was in 1850 that he announced the preparation of compounds of zinc with methyl and ethyl, and predicted the existence of twenty other similar bodies. Intrinsically interesting as are these substances, their importance lies rather in the theoretical deductions which he drew from a consideration of their composition. In this way he evolved the conception that the atoms of zinc, tin, &c., had only room, so to speak, for the attachment of a fixed and definite number of the atoms of other elements; and this hypothesis, which was communicated to the Royal Society in 1852, was the basis of the doctrine of atomicity or equivalence of the elements which may be said to have dominated the course of all subsequent chemical theory since its enunciation. These views, together with others that followed from them, shared the usual fate of new ideas in failing to command universal and immediate acceptance; and that Frankland did not always receive full credit for them may be ascribed to the fact that, in the discussion of their value, their authorship was sometimes forgotten and other men came to be looked upon as their originators. This result was probably due in part to Frankland's standing aloof from

the controversies that arose, and to his general objection to self-advertisement, which it is permissible to say he sometimes carried so far as to shrink from legitimate self-assertion.

In applied chemistry, his first piece of work was begun in 1851, when he was appointed Professor of Chemistry in Owens College, Manchester, and related to the manufacture of water-gas. He also investigated the chemical composition of the gases evolved from different kinds of gas-coal, and incidentally invented a form of gas-burner which—like many other old inventions—has recently been brought forward as something new. By using two concentric chimneys, he made the waste heat of the flame raise the temperature both of the gas and the air consumed by the burner to 500 or 600° F., and so ensured a much more efficient light. But his most important contributions to applied chemistry had reference to water supply and sewage questions. When in 1865 he succeeded Hofmann as Professor of Chemistry at the Royal College of Chemistry (Royal School of Mines) he undertook to continue the monthly analysis of the water supplied to the metropolis, which Hofmann had begun a few months before for the Registrar-General. These monthly analyses, it may be mentioned, he continuously performed ever since that date, and his comments and reports form a most interesting and valuable feature of the Registrar-General's mortality returns in which they are to be found. This task involved the elaboration of a new method of water-analysis, since the processes then known he found seriously imperfect and untrustworthy, especially for the detection of pollution by sewage or animal matters, and it was only after two years of laborious experiments, in which he was helped by his then pupil, Professor H. E. Armstrong, that he succeeded in devising means with the accuracy of which he was satisfied. In 1868 he was appointed a member of the second Royal Commission on the Pollution of Rivers, and the Government provided him with a splendidly equipped laboratory in which to carry out the inquiries necessary for the purposes of that body. These researches occupied six years, and that they were on a most elaborate and exhaustive scale is sufficiently shown by the long list of subjects investigated. Among these were the chemical qualities of water from various geological strata and from different sources of supply, such as lakes, rivers, wells, &c.; the possibility of rendering water once polluted again wholesome; the propagation of disease by drinking water; the influence of hard water on health; the deterioration of water in mains and service pipes; and the quality of London water taken from the Thames. Of the last he did not at that time at all approve, because he held the belief that, no matter how satisfactory might be the chemical purification of polluted water by domestic or other artificial filtration, there was evidence that such water was still capable of propagating epidemic diseases. But this opinion was profoundly modified in the course of time as filtration became better understood and more effectively applied. Lecturing before the Royal Institution in 1896, he declared unequivocally in favour of the Thames as the source of water supply for London, and, after emphasising the astounding effect of sand filtration as practised by the London companies upon the living matter contained in raw river water, said that, with the provision of the storage reservoirs recommended by the Balfour Commission, London would possess an ample water supply, unsurpassed for palatability, wholesomeness, and general excellence. The purification of sewage and the means of preventing the pollution of rivers by trade refuse, &c., were among the other matters he investigated in connexion with the Commission.

Sir Edward Frankland was one of the few men who have spent a night on the very summit of Mont Blanc. This he did in August, 1859, in company with Tyndall, and the circumstance proved the starting-point for a long series of investigations in physical chemistry. On the summit the rate of combustion of stearin candles was observed, with the object of discovering whether the rate of burning of bodies needing a supporter of combustion is independent of the density of the atmosphere in which they are burnt—a question which was answered in the affirmative. But Frankland noticed that the candles gave a very feeble light, and this observation induced him on his return to England to institute a series of experiments on the source of light in luminous flames. The results led him to believe that the light was not always due to solid particles, since many luminous flames had none, and he showed that incandescent gases and vapours emit light in proportion to their density—hydrogen, for example, having a luminous flame, if burnt in a pressure of 10 or 20 atmospheres. Other experiments, in which Sir Norman Lockyer also had a share, he regarded as showing that brilliancy of light and continuity of spectrum are not peculiar to ignited solid or liquid matter, but that the same phenomenon is produced by the ignition of compressed gases. A consequence of this discovery was the conviction that the sun cannot be ignited solid or liquid matter, but that, at least, the photosphere, or outer layer of luminous matter, must consist of gases or vapours only.

In physiological chemistry he took part in a crucial experiment to settle the vexed question of the origin of muscular power. He, Fick, and Wislicenus, proposed to confine themselves to a non-nitrogenous diet and ascend the Faulhorn, taking a strict account of the greatest possible muscular oxidation by determining the amount of nitrogen expelled from each body before, during, and after the ascent. In the end, however, he was unable to make the experiment on his own person, but Fick and Wislicenus performed the ascent while he did the difficult laboratory experiments and calculations necessary for the interpretation of the results. The latter, in his opinion, left little room for doubt. He thought it impossible to account for more than a small fraction of the work done in the ascent by the force evoked by the transformation of muscle into the quantities of its products observed by the experimenters, and he concluded that a large proportion at least of the force was developed by the oxidation of non-nitrogenous substances, such as fat.

A few personal details of his life may be added. He held professorships of chemistry successively in Owens College, St. Bartholomew's Hospital, the Royal Institution, where he followed Faraday, and the Royal College of Science, South Kensington, retiring from the last in 1885. The Royal Society, which made him a Fellow in 1853, gave him a Royal medal in 1857, and he also acted as its foreign secretary. Abroad, the French Academy of Sciences recognised his merits by making him a corresponding member in 1866, and he was also a foreign member of the Academies of Sciences of Bavaria, Berlin, St. Petersburg, Upsala, America, and Bohemia. Oxford gave him the degree of D.C.L. in 1873, and Edinburgh that of LL.D. in 1884. He was the first president, in 1877, of the Society of Chemical Industry, and served as president of the Chemical Society in 1871, being one of the six ex-presidents entertained at the recent banquet. The honour of K.C.B. was bestowed on him in 1897.

He was twice married, first to Sophie, daughter of Herr F. W. Fick, of Hesse-Cassel, who died in 1874, and second in 1875 to Ellen Frances, daughter of Mr. C. K. Grenside, of Wimbledon. She also predeceased him. Professor Percy Frankland, of Birmingham, is the second son of the first marriage.—*The Times.*

PROFESSOR ATTFIELD contributes the following to a contemporary:—

"The Editor asks me for personal reminiscences of my old chief Frankland, whose death all science is deploring. For five years, 1857 to 1862, I was, as Demonstrator, daily with him as Lecturer in Chemistry at St. Bartholomew's Hospital Medical School, and I was his lecture-assistant and one of his research-assistants either at the Hospital, the Royal Institution, or the Military College,

Addiscombe; so that during the period mentioned I saw a great deal of nim. My first quarter of an hour with him—at Owens College, Manchester, at the time of the Art Treasures Exhibition, 1857, and within a week of his appointment to Bartholomew's, where I had already been under Stenhouse for three years—revealed his great powers of perception and his transparent simplicity and nobility of character. Within twenty minutes he had found enough in me for reliance, I enough in him to make me long to work under him. Yearly my respect for him deepened. To his students he was ever approachable, patient, and informing; to his colleagues ever genial, loyal, and chemically and physically helpful. The world knows of his ability as a chemist and physicist; but he was a skilled mechanic also, an admirable worker in metal, wood, and glass. In his prosecution of research and the publication of his discoveries his one aim seemed to be the revelation of truth, never the glorification of self. The why and the wherefore, the whence and the whither, seemed always to beckon him, and if ever he turned aside at the earnest request of clients it was only a case of *reculer pour mieux sauter*. 'We must live,' he used to say, with something between a smile and a sigh. To his helpers he was kind, yet firm—the kinder because firm—in his demands for accuracy. While assisting him in experimentally ascertaining the effect of diminished atmospheric pressure on combustion, it needed effort to get from him his personal experience in ascending Mont Blanc and spending a night on its summit; but what he told me implanted in me that form of joy in the beautiful which mountains, little and big, chiefly the former, afterwards afforded me for five and twenty years, and which is not excelled by any of the joys of earth. He turned over to me the conduct of the Hospital school class in practical chemistry, and encouraged me to print the results of my educational experience. Against his own interest, as he said, he exerted himself to secure my election to a professorship at the Pharmaceutical Society in 1862, and when, a year afterwards, I confided to him my disappointment that a certain Committee had refused me an induction coil with which to carry on my researches on the spectra of electrically ignited gases in semi-vacuous tubes, he reminded me, in spite of his love for pure science, that I had been chosen instead of three men of greater experience in research because of my greater knowledge of the applications of chemistry to pharmacy, and that I must order my life accordingly. Through him I had become known to men like Faraday and Tyndall, Geissler and Casella, Kolbe and Strecker, Gassiot and Playfair, men who gave me help through their respect for Frankland. His advice, and letters of introduction to two Universites, much aided me in obtaining a degree. It was he who invited me to become a candidate for the Fellowship of the Royal Society. Small wonder that I loved him. The powerful searchlight of his brain could all but reveal the atoms of matter, could illumine the photosphere of the sun, could penetrate corners in vitality; Nature's forces yielded up their secrets under its influence, welcoming it as a sister to themselves. Yet he was unselfish and sympathetic, not kinder to me than to all by whom he was immediately surrounded. Alas! he has gone.

"JOHN ATTFIELD.

"Watford, August 15, 1899."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 3. July 17, 1899

Combination of Carbon Disulphide with Hydrogen and Nitrogen. — M. Berthelot. — When a mixture of hydrogen and carbon disulphide is submitted for some time to silent electric discharge, the hydrogen is absorbed and a compound appears to be formed having the formula $C_2H_2S_4$. This may represent either oxalic acid in which the oxygen is replaced by sulphur, or a persulphide derived from glycollic aldehyde. The same set of experiments were tried with nitrogen instead of hydrogen. In the two experiments the proportion of nitrogen and carbon disulphide was $4CS_2 : N_2$ and $7CS_2$ to N_2.

Compounds of Nitrogen with Oxygen.—M. Berthelot.—During the process of purifying argon from nitrogen, the author measured the proportion between the nitrogen and oxygen as the mixture is subjected to the electric discharge. The results are interesting, as showing the successive and gradual formation of the different oxides of nitrogen. It appears that gaseous nitrous acid is always formed first, even in the presence of an excess of oxygen, and that it only changes into peroxide of nitrogen very slowly. The dioxide of nitrogen formed under the action of the electric spark on the mixture of nitrogen and oxygen combines, first with one atom of oxygen, forming nitrous anhydride, $2NO+O=N_2O_3$; then it unites with a second atom of oxygen, forming peroxide of nitrogen, $N_2O_3+O=2NO_2$.

Chromic Acetate.—A. Recoura.—The author describes the isomeric forms of chromic acetate. These compounds are particularly interesting:—(1) Because chromic acetate shows four isomeric forms, the other salts but two; (2) because whilst in the preceding salts the form stable in solution is the normal salt, in the case of the acetates the stable forms are those which are not true salts. The formula $Cr(C_2H_3O_2)_3$ is taken for chromic acetate. The preparation and properties of the various forms are described.

Journal de Pharmacie et de Chimie,
Series 6, Vol. ix., No. 4.

A New Method for the Estimation of Carbonic Oxide. — MM. Schlagdenhauffen and Pagel. — Inserted in full.

The Alteration of an Iodoformed Lint.—P. Rouvet. —The author has observed that iodoformed lint undergoes an alteration after keeping. On opening a packet an odour of putrefying organic matter was observed; the oiled parchment paper in which it was wrapped had a dark brown tint and was specked with small brilliant white crystals. By micro-chemical and ordinary reactions these crystals were found to consist of iodide of zinc, showing that the iodoform had been reduced, as they were the result of the iodoform vapour, or hydriodic acid, on the galvanised iron case in which the lint had been packed. The oiled parchment paper was also connected with the alteration, and the author recommends that paraffined paper should be substituted in future.

No. 5.

The Detection and Estimation of Bromoform in Toxicology.—A. Richaud.— In detecting bromoform in the presence of organic matter by entanglement with a current of steam, we are able to collect, almost integrally, all the bromoform in a quantity of water not exceeding 75 to 100 c.c. It then suffices to add a few morsels of potash, to fit the flask with a vertical refrigerator, and heat gently for an hour or an hour and a half to completely transform the bromoform into bromide.

No. 6.

On the Nitrated Gaïacols.—H. Cousin.—Two nitrated gaïacols are known—the 4-nitrogaïacol prepared by H. Rupe by the action of nitric acid on 4-nitrosogaïacol, and a dinitrated gaïacol (4 : 6-dinitro-gaïacol) obtained by Hertzig by the action of a current of nitrous vapours on an ethereal solution of gaïacol. The author has employed two new methods for preparing these de-

r vatives:—5 c.c. of crystallised gaïacol are dissolved in 50 c.c. of chloroform, then gradually add—while keeping the liquid cool—a mixture of 5 c.c. of fuming nitric acid and 20 c.c. of glacial acetic acid; to the dark brown liquid 200 c.c. of water are added, and the chloroformic layer collected. On evaporation, a reddish brown crystalline mass is left, which is purified by several crystallisations in alcohol at 50°; this is identical with the body found by Hertzig. The mononitrated gaïacol was prepared by dissolving 10 c.c. of acetyl-gaïacol, or of acetic ether of gaïacol, in 10 c.c. of glacial acetic acid, and gradually adding a mixture of 10 c.c. of fuming nitric acid and 10 c.c. of acetic acid; a lively reaction takes place, nitrous vapours being given off. After cooling, water precipitates a solid material, which is drained by the filter-pump and purified by crystallisation in alcohol at 90°. In this manner a mononitrated acetyl-gaïacol is obtained in the form of fine, nearly white needles, insoluble in water, soluble in boiling alcohol, fusing at 100—101°.

The Action of Amylic Alcohol of Fermentation on its Soda Derivative.—M. Guerbet.—One kilogrm. of amylic alcohol and 130 grms. of sodium are placed in a flask fitted with a vertical condenser and heated gradua ly until boiling; this is kept up for twenty-four hours, and the mass taken up with water; add sulphuric acid, but leaving the solution still slightly alkaline, remove the supernatant oily layer, wash it with water, and dry over carbonate of potassium. After several rectifications, 125 grms. of a neutral liquid, boiling at 210—211°, can be separated. There remains in the flask a small quantity of an oily compound from which 10 grms. of a neutral liquid can be separated, boiling at 173—175° under 8 c.m. pressure. To the alkaline solution left, add an excess of sulphuric acid, when a mix ure of acids is formed, which is dried over sulphate of soda; of these, isovaleric acid is the principal. These three compounds—the alcohol ($C_{10}H_{22}O$), the acid ($C_{10}H_{20}O_2$), and isovaleric acid—result, no doubt, from the action of amylic alcohol on its soda derivative; one molecule of each of these compounds will react on the other according to the equation $C_5H_{11}NaO + C_5H_{12}O = C_{10}H_{22}O + NaOH$, and the soda thus formed oxidises the amylic alcohol by the reaction $C_5H_{12}O + NaOH = C_5H_9NaO_2 + 4H$.

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THE CHEMICAL NEWS.

Vol. LXXX., No. 2074.

SOME DRAWBACKS TO THE USE OF ACETYLENE.

By Prof. J. VÉRTESS.

While coal-gas has had to struggle for a whole century before becoming the almost universal lighting agent, its rival, acetylene, has already—after only a short time—achieved a certain success. Of course acetylene is not a newly discovered body, but it is only since the economic production of carbide of calcium that it has become practicable as a lighting agent.

Theoretically the production of acetylene is a very simple matter, but such is not the case practically.

Carbide of calcium, as is well known, is a black, crystalline, very hard material, not decomposed by heat, but easily decomposed by water into acetylene and lime. It has a density of 2·2, and it is not soluble either in petroleum or in benzene.

Concentrated acids have no action on it.

Acetylene consists of a colourless gas, with a penetrating odour of garlic. Its density is 0·1; 1 litre of acetylene weighs 1·16 grms. It is easily soluble in water, and can be liquefied at 0° under a pressure of 48 atmospheres. In this state it is very explosive. It burns with a white flame, without a dark cone; the temperature of this flame is lower than that of coal-gas.

Unfortunately, lighting by acetylene still presents numerous difficulties, to which I am desirous of calling the attention of specialists and others, now that I have had the opportunity of examining the installation which supplies the town of Veszprim in Hungary.

Let us first consider the carbide, the source of all the trouble. This body is never pure, but always contains at least 20 per cent of impurities. Theoretically, 64 parts by weight of carbide should give 26 parts by weight of acetylene,—that is to say, that 1000 grms. of carbide ought to produce 406·25 grms. of acetylene, and, as 1 litre of this gas weighs 1·16 grms., we ought to get 350 litres. But the continental factories will not guarantee a return of more than 300 litres, and practical experience shows that we can hardly depend on more than 280 to 290 litres. It is true that the estimation of the return is not free from causes of error, inasmuch as during the weighing the carbide absorbs a certain amount of moisture from the atmosphere; this causes a loss of acetylene. But the small errors which result, when calculated on 1000 grms. of material, are multiplied in proportion. We are obliged to work with small quantities, seeing that only 100 grms. of material give off 30 litres of gas, and it is difficult to arrange graduated gas-holders to store such large quantities. Further, the carbide is so little homogeneous that several samples must be tested and examined in order to obtain a mean value. If, on the other hand, we only take 10 grms., the error resulting from the disengagement of acetylene in the air will be multiplied one hundred times if the results are calculated, as they should be, on 1000 grms. I have examined the manner in which the carbide behaves in the presence of acids, and I found that concentrated sulphuric acid has no action on this body; but no matter how little water the acid may contain, bubbles of gas are formed until the whole of the water is consumed. This property of the carbide of not being attacked by concentrated sulphuric acid enables us to estimate its producing power of acetylene. I have made several experiments in this direction, and the results obtained were fairly correct and concordant.

I must here again mention that the carbide contains sulphur, phosphorus, and nitrogen, from which it results that the acetylene will be contaminated with sulphuretted hydrogen, phosphoretted hydrogen, and ammonia. The acetylene must therefore be purified to the same extent as is coal-gas, for fear that its use in closed places might cause serious accidents.

But the greatest drawback of all is that acetylene burns with a smoky flame. Certainly the flame does not smoke at first, but after 200 or 300 hours smoke begins to be formed. This is caused by the burners attaining a temperature higher than that of the decomposition of acetylene, and thus the gas is decomposed into carbon and hydrogen.

I have also noticed a very curious phenomenon in the gas-pipes; I there found a deposit of finely-divided carbon like soot. I also found a very remarkable liquid condensation, consisting of carbides of hydrogen. These bodies are also formed in the generators, whence the necessity of using syphons. We thus see that it is quite erroneous to imagine that acetylene does not require purifying.

There is still another inconvenience resulting from impurities contained in acetylene. It is by no means uncommon to see, in a closed place, a sort of fog fill the room after a longer or shorter interval. What is the cause of this phenomenon? The acetylene is decomposed in the burner, the carbon is deposited while the hydrogen burns, giving rise to the formation of watery vapour; and it is this, in conjunction with the ammonia, the sulphuretted hydrogen, and the phosphoretted hydrogen, which produces the fog, causing headache and nausea.—*Chem. Zeitung*, 1898, p. 174.

THE ANALYSIS OF ACETYLENE.

By WALTHER HEMPEL and LEOPOLD KAHL.

Among the impurities which accompany acetylene, the most important—after the oxygen and nitrogen of the air—is phosphoretted hydrogen. As calcium carbide leaves on decomposition a residue formed principally of calcic hydrate, carbide and silicide of iron, and carborundum—that is to say, a residue with a strongly alkaline reaction—it is certain that acetylene does not contain any sulphur in the form of sulphuretted hydrogen. It is true that some writers have noticed the presence of a small quantity of sulphur, but it is probable that it existed in the state of sulphurised organic compounds. A sample of calcium carbide from New York which we analysed contained from 6 to 8 per cent of carborundum and silicide of iron, and 0·2 to 0·24 per cent of silica.

As the presence of hardly noticeable quantities of phosphoretted hydrogen may make the acetylene spontaneously inflammable, it is of the greatest importance to entirely eliminate this body. This could be done by using only a carbide free from phosphorus, or by purifying the acetylene by means of suitable reagents. In any case it is necessary to have methods of gas analysis enabling us to estimate rapidly and exactly the quantity of phosphoretted hydrogen present in the acetylene.

Lunge (*Zeit. Anorg. Chem.*, 1897, p. 651) has recently proposed decomposing, by means of water, known quantities of carbide and passing the acetylene produced through sodic hypochlorite. The phosphoretted hydrogen is thus oxidised to the state of phosphoric acid, which is easy to estimate by ordinary gravimetric means. It is certain that this method gives very exact results, but unfortunately it requires too long a time. In our opinion it is essential to have a method permitting the volumetric separation of the acetylene from the phosphoretted hydrogen, so that the analysis can be finished in a few minutes.

Such is the problem we proposed to solve, and with this view we have tried a large number of solutions which might lead us to the desired end. We prepared a fairly large quantity of phosphoretted hydrogen by heating an

alcoholic solution of potash lye with white phosphorus, the gas produced being collected in a glass gas-holder. As this phosphoretted hydrogen contains a fairly large proportion of hydrogen and a little air, the figures given below will not be found to be of scientific accuracy. The acetylene was freshly prepared for each series of experiments.

To put the gas in contact with the reagents we operated in the following manner:—Into a pipette filled with mercury we introduced 1 c.c. of the reagent and then 100 c.c. of gas; after having shaken vigorously for three minutes, we measured in a gas burette the fraction unabsorbed.

The figures in the following table show the quantity of gas absorbed by 1 c.c. of the reagent.

Reagent used.	Phosphoretted hydrogen absorbed. C.c.	Acetylene absorbed. C.c.
I. 1 c.c. of cuprous chloride in hydrochloric solution prepared by C. Winkler's method	39·8	9·4
II. 1 c.c. of cupric chloride in hydrochloric solution, obtained by dissolving 10 grms. of crystallised cupric chloride, $CuCl_2,2H_2O$, in 100 c.c. of water and 5 c.c. of concentrated hydrochloric acid	8·6	5·2
III. 1 c.c. of cupric sulphate in sulphuric solution, prepared by dissolving 15·6 grms. of crystallised cupric sulphate, $CuSO_4,5H_2O$, in 100 c.c. of water and 5 c.c. of sulphuric acid at 25 per cent by volume	8·8	0·2
IV. 1 c.c. of sodic hypochlorite, prepared by dissolving 10 grms. of crystallised carbonate of soda in 100 c.c. of water, adding an excess of chloride of lime, and filtering	3	0·6
V. 1 c.c. of sodic hypobromite, prepared by dissolving 100 grms. of caustic soda in 1250 c.c. of water and adding 25 grms. of bromine	Explosion.	
VI. The preceding solution diluted with four volumes of water	—	1·3
VII. Sodic hypochlorite, prepared by passing chlorine gas through soda-lye. This reagent was brought, by the addition of caustic soda and water, to the same alkalimetric titration and the same value in active chlorine as Solution V.	—	0·7
VIII. Permanganate of potash at 5 per cent.	3·2	2·6
Permanganate of potash at 1·25 per cent	1	1·2
IX. Nitrate of silver at 3 per cent	—	1·6
X. Cupric sulphate in nitric solution, obtained by dissolving 78 grms. of sulphate of copper, $CuSO_4,5H_2O$, in 250 c.c. of water and 250 c.c. of concentrated nitric acid .	1·2	0·8

As can be easily seen, the sulphate of copper in sulphuric solution is the best reagent for separating phosphoretted hydrogen from acetylene.

A large number of trials made with the view of effecting the absorption in gas pipettes has shown us that light has a great influence on the results obtained. We have attempted to prepare in a double gas pipette filled with acetylene a solution of cupric sulphate saturated with acetylene; but when left to itself the cupric solution continued to absorb fresh quantities of acetylene, even in diffused light. The same phenomenon occurred with sodic hypochlorite.

Following up our researches, we eventually found that acetylene behaves differently, according to whether it is put in contact with cupric sulphate only or with cupric sulphate and metallic mercury in the presence of phosphoretted hydrogen. We found that, in the presence of mercury and an excess of cupric sulphate, the diminution of volume due to absorption is exactly four times greater than the volume of the phosphoretted hydrogen present.

It was therefore important to know if acetylene free from phosphoretted hydrogen would behave in the same manner, and we found that in both cases the result was the same—2 c.c. of cupric sulphate in acid solution absorbed 0·4 c.c. of gas.

We give below the results obtained with a mixture of acetylene and phosphoretted hydrogen at 52·4 per cent. The gaseous mixture was well shaken up with 3 c.c. of a sulphuric solution of cupric sulphate saturated with acetylene. The small differences are partly due to the difficulty experienced in always saturating the reagent with the same quantity of acetylene.

Acetylene used.	Phosphoretted hydrogen at 52·4 per cent used.	Diminution in volume found.	Actual phosphoretted hydrogen.	Phosphoretted hydrogen found by absorption, admitting that the phosphoretted hydrogen equals a quarter of the diminution of volume.
92·8	5·6	11·2	2·9	2·8
90·2	7·4	13·4	3·9	3·4
94·6	2·4	4·6	1·2	1·15
92·2	5·2	10·6	2·7	2·65
94·0	3·2	8·3	1·67	2·0
82·0	5·4	11·0	2·82	2·75

To sum up, for determining the quantity of phosphoretted hydrogen contained in acetylene, the gas is measured in a gas burette filled with mercury, and from thence transferred to another burette filled with mercury and 3 c.c. of cupric reagent saturated with acetylene. After shaking for three minutes, the volume of the unabsorbed gas is measured; a quarter of this volume represents the phosphoretted hydrogen present.—*Zeit. f. Angew. Chem.*, 1898, No. 3, p. 53.

THE ESTIMATION OF OXYGEN IN COPPER.

By MAURICE LUCAS.

In this paper I have only dealt with the estimation of suboxide of copper in commercial copper.

Such copper now-a-days generally contains only very slight traces of foreign matters, but it always contains a notable quantity of oxygen, on which different observers are far from being in accord; and if analysis is admitted to be a gauge of the quality of a copper, the estimation of this oxygen is very necessary.

It is combined to a great extent with the copper in the state of suboxide of copper, Cu_2O; the proportion of oxygen combined with metals other than copper, and with the metalloids, is negligible, except sometimes in the case of arsenic, which is generally admitted to be in the state of arseniate of copper or of lead.

It is impossible to have a complete check of the esti-

mation of suboxide of copper, because we cannot effect the synthesis of the melted mixture, copper—suboxide of copper.

It is for this reason that I have compared the results obtained;—1st, by heating in hydrogen and measuring the loss of weight; 2nd, by attacking with nitrate of silver and estimating the insoluble residue.

I have varied one by one the conditions under which this latter method was carried out, and have finally decided on a series of operations which satisfies the following conditions:—

a. Constant results with the same sample.
b. No variations with the sample taken.
c. Close agreement with the reduction by hydrogen.
d. No result with copper electrolysed by M. Riche's method.
e. By attacking the suboxide only, the quantity of copper contained in the residue is well in *rapport* with M. Hampe's formula.
f. The simultaneous attack of the copper and of the suboxide gives the same results as if the attacks were conducted separately.
g. If a strip of copper is placed in neutral nitrate of copper, it does not on filtration leave any precipitate containing copper.

Samples used.—The experiments were carried out on a test sample of copper to which 3 per cent of suboxide of copper had been added while melted (2·75 per cent remained), and on a sample of calumet copper. These two samples did not contain sulphur or arsenic, and only 0·001 per cent of lead and iron.

I. *Reduction by Hydrogen.*

This method of estimation did not appear to me to be a trustworthy check, for, in order to make certain that the reduction is complete, it is necessary to test for any suboxide remaining—that is to say, to admit *à priori* an error in the method of analysis. Nevertheless, it has been done by closely following Hampe's instructions (*Zeit. Anal. Chem.*, vol. xiii., p. 188; Fresenius, "Anal. Quant.," p. 1018), and gave the following results:—

Test copper	2·75
Calumet copper	0·68

and, by fusing the latter in hydrogen, 0·75.

The coppers thus reduced to a constant weight were assayed by Hampe's method modified; they did not then contain any suboxide.

II. *Attack by Nitrate of Silver.*

Hampe's Method.—Hampe showed that by the action of nitrate of silver the copper was dissolved, and the suboxide transformed into basic nitrate of copper according to the formula:—

$$3Cu_2O+3AgO.NO_5+nHO=$$
$$=(4CuO,NO_5+3HO)+2(CuO.NO_5)+3Ag+(n-3)HO.$$

This basic nitrate is the same as that obtained by Gerhardt by boiling the neutral nitrate with the oxide CuO or an alkali.

The copper in the insoluble residue is estimated, and by following Hampe's method very closely we obtained—

Test copper .. .. .. 2·88.

Hampe's Method modified.—The solution of nitrate of silver is prepared by attacking silver with nitric acid and continuing the crystallisations until the mother-liquors are no longer acid; the crystals are dried over quicklime and protected from the light; a 5 per cent solution was prepared from these crystals, allowed to stand for a time, then decanted into a red glass flask.

Strips of copper of about 0·15 m.m. thickness, carefully rolled, and cleaned with glass paper, are attacked, using about 1 grm. of copper to 120 c.c. of the solution, for fifteen hours *in vacuo*, without shaking. The residue is filtered on a plug of asbestos and washed with cold water until no more copper passes through. The residue is again attacked for two hours *in vacuo*, and a test made to find if any more copper has been dissolved; this residue is now filtered, washed, and attacked with nitric acid. The silver is separated by hydrochloric acid, and the copper estimated by electrolysis and its weight multiplied by 1·689; it must be tested to make sure that it contains no silver.

The following results were obtained by this method:—

	Weight of sample.	Suboxide of Cu per cent.
Test copper ..	10 grms.	2·75, 2·78
	1 grm.	2·70, 2·76, 2·71, 2·74, 2·65, 2·79
Calumet copper	10 grms.	0·63, 0·65
	1 grm.	0·68, 0·68, 0·68.

The copper was also estimated colorimetrically, by means of ferrocyanide of potassium, a method which is found to be the most convenient for the small proportions which are generally present. In a future paper I shall point out the necessary precautions to take. By this method I have obtained the following results:—

	Cu_2O per cent.	
	Rolled strips.	Turnings.
Calumet copper.. ..	0·68, 0·69	0·69
Société des Metaux:—		
Electrolytic copper from Bornel	0·49, 0·49	0·52
Civet copper marked N.A.	0·40, 0·48	0·52
Société de Biache St-Waast:—		
Electro copper	0·76, 0·77, 0·78	0·78
Arizona copper ..	0·34, 0·34, 0·34	0·34
Boléo copper	0·80, 0·70, 0·76, 0·72	0·78

III. *Conditions for Working.*

The following assays were made with two samples, but only making one variation at a time from the method adopted above; they serve to justify the precautions recommended.

Sample taken.—I have noticed that, by diminishing the amount of the sample used, the results given by Hampe's method were progressively increased; I thus obtained as much as 6 per cent on the test copper.

The modified method did not show such irregularities.

Solution of Nitrate of Silver.—Nitrate of silver is reduced by light and becomes acid; we cannot correct its acidity by adding silver; the addition of caustic soda introduces carbonates, the inconvenience of which we shall see later on.

The assays made with 50 per cent nitrate of silver solution gave results both low and irregular; the silver was in compact morsels. The action is too rapid, and is impossible to regulate.

Treatment of Turnings.—The treatment of turnings generally gives results identical with those from rolled strips, but we can never be quite certain that no oxide is present on the surface. It is for this reason that I prefer to use rolled strips.

Copper melted in an atmosphere of hydrogen, and rolled thin, is completely dissolved by nitrate of silver, which shows that rolling, when carefully done, does not imprison any oxide in the metal.

Attack in the presence of Air.—These results are always higher (3·15 instead of 2·75). Now:—

1st. By exposing a neutral aqueous solution of nitrate of copper to the air, filtering on asbestos, and washing with cold water, the asbestos does not take any colour on adding ferrocyanide of potassium.

2nd. The same is the case with a mixture of neutral nitrate of copper and nitrate of silver.

3rd. But if 3 grms. of precipitated silver are added to the neutral nitrate of copper, and the liquid filtered, after twenty-four hours' contact with the air, 0·003 grm. of copper is found on the asbestos; this is precisely the

difference between the quantities of copper weighed to obtain 3·15 and 2·75 per cent. of suboxide of copper in 1 grm. of test copper.

Attack in the presence of Carbonic Acid.—In a current of carbonic acid, or even simply in an atmosphere of carbonic acid, we obtain too low results (0·7 instead of 2·75); copper is dissolved.

A current of carbonic acid through water holding in suspension the hydrate, carbonate, or the basic nitrate of copper, dissolves as much as 0·034 grm. of copper per litre, which is re-precipitated on boiling or by exhaustion under the air-pump. Caustic soda, which generally contains carbonates, must not be used for correcting the acidity of nitrate of silver.

Attack in the presence of Hydrogen.—With a current of hydrogen, or simply in an atmosphere of hydrogen, the results obtained are too low (1·8 instead of 2·75).

Attack in the presence of Nitrogen.—With a current of nitrogen in a liquid freed from air, we obtain good result: this process *in vacuo* has the advantage of making the action more rapid by agitation.

Filtration.—Filtration through paper gives higher results than filtration through asbestos. If we filter the neutral nitrate of copper successively through several filter-papers, it is noticed that in spite of the most prolonged washings, which eventually do not carry off any copper, all the filter-papers are still coloured red by ferrocyanide of potassium: this does not occur when using either asbestos or glass-wool.

The quantity of copper, which is variable, does not exceed 2 m.grms. for 10 c.m. of filter-paper.

Washings.—These washings, which do not present any difficulty, take a very long time when we operate on 10 grms.; it is for this reason that I have adopted 1 grm. as sufficient to work on.

Solution of the Basic Nitrate of Copper.—Independently of the process I have just described, we can effect the solution of the basic nitrate of copper by warm dilute sulphuric and hydrochloric acids, or by ammonia. Hydrochloric acid at 5 per cent dissolves both more copper and less silver; it should be used in two successive portions. —*Bull. Soc. Chim.*, Series 3, vol. xix.-xx, No. 16-17.

SEPARATION OF PROTEID BODIES FROM THE FLESH BASES BY MEANS OF CHLORINE AND BROMINE.

By H. W. WILEY.

In dry, finely-ground animal matters, from which the fats have been thoroughly extracted with ether, it is possible to effect an easy separation of the nitrogenous bodies into three groups. These groups, for purposes of dietetic study, are sufficiently distinct to afford a safe basis of valuation of the different nitrogenous constituents. The process which has been adopted in the laboratory of the Division of Chemistry, Department of Agriculture, for this separation is given in detail here.

Details of Method.

In the dry, fat-free, finely-ground animal substance the nitrogenous bodies soluble in water may be separated by first thoroughly exhausting the material with cold or lukewarm water, and afterwards with water near the boiling temperature. By this method the water-soluble constituents of the nitrogenous substances are thoroughly removed. Having determined the total percentage of nitrogen in the whole sample, the residual insoluble nitrogen is determined in the residue left after extraction. This percentage multiplied by 6·25 gives the total quantity of insoluble proteid matter contained in the animal material. In the filtrate the soluble proteid matter which has been dissolved by the water may be completely thrown out of solution by treatment with bromine in the manner about to be described.

About 1-grm. portions of the dry animal material are washed with ether by decantation, using from 50 to 100 c.c. of ether for each sample, and decanting the ether through filters which are afterwards used to receive the portion of the sample insoluble in hot water. After allowing the ether to evaporate, the samples are treated first with cold and then with hot water, this washing also being by decantation, the total amount of water used being from 300 to 400 c.c. The undissolved residues are brought on to the filter with the last portions of water. The nitrogen in the residues on the filters is determined by the Gunning method.

The filtrate from the insoluble portions of the meat is received in Kjeldahl flasks and used for the separation of the soluble proteid nitrogen by bromine. The filtrate is first acidulated with two or three drops of strong hydrochloric acid, and then about 2 c.c. of liquid bromine are added and the contents of the flask vigorously shaken. If the bromine be all taken up more is added until finally a globule of ½ c.c. of liquid bromine is left undissolved and the supernatant liquid is thoroughly saturated with bromine. The mixture is then allowed to stand overnight, by which time the precipitate will have settled. The supernatant liquor is passed through the filter and the precipitate in the flask washed by decantation with water, the globule of undissolved bromine serving to saturate the wash water so that it is unnecessary to use additional bromine water for the washing. The filter containing the precipitate is returned to the same flask in which the precipitation has taken place, and the nitrogen therein determined by the Gunning method. The sum of the nitrogen in the part insoluble in water and the part precipitated by bromine is subtracted from the total nitrogen determined on the original sample, and the difference gives the total nitrogen in the flesh bases.

Factors for Calculation of Total Nitrogen.

The factors used for calculating the total nitrogenous bodies are as follows:—

For the part insoluble in water, $N \times 6{\cdot}25$

For the part soluble in water and precipitated by bromine, $N \times 6{\cdot}25$.

For the flesh bases, $N \times 3{\cdot}12$.

This method is based upon investigations reported by Rideal and Stewart (*The Analyst*, 1897, xxii., 228 *et seq.*) last year.

These writers recall some of the experiments made in 1876, in which it was shown that a current of chlorine gas, conducted through an aqueous solution of proteid matters, produces a precipitate which is of a quite constant composition, and one which can be collected, dried *in vacuo*, and weighed. They describe particularly the use of this reagent in precipitating gelatin prepared from the high-grade commercial article. They show that the total quantity of gelatin can be accounted for from the weight of the precipitate by multiplying the weight of the precipitate obtained by the factor 0·78. The authors also point out the possibility of using bromine for chlorine for the precipitation, and state that the studies of the use of bromine are under way. They call attention to the fact that as early as 1840 chlorine had been used by Mulder for the precipitation of soluble proteids, and refer to a paper of his published in Berzelius's *Jahresbericht*, vol. xix., p. 734, in which he states results on precipitation quite similar to those secured by Rideal and Stewart.

At the close of their paper Rideal and Stewart mention the work in this direction of De Vrij (*Ann. Pharm.*, lxi., 248), Thénard (*Mém. d'Arcueil*, ii., 38), Mulder (*Bulletin en Néerlande*, 1839, 153), and Berzelius (*Jahresbericht*, xix., 729), on the same subject.

Allen and Searle (*The Analyst*, 1897, xxii., 258—263), acting on the suggestion of Rideal and Stewart, worked out the bromine method by applying it to various soluble proteids, including the whole range from albumen to

peptone. In the application of this test to commercial gelatin the following process was employed:—

Fifty grms. of commercial gelatin were dissolved in warm water and the solution diluted to half a litre. In 10 c.c. of this solution, corresponding to 1 grm. of the gelatin, the nitrogen is determined directly by the Gunning-Kjeldahl process. Another portion of 10 c.c. is treated with an excess of bromine in the following manner:—

The solution is first brought to a volume of 100 c.c. with water, and placed in a conical beaker with a sufficient quantity of hydrochloric acid to produce distinct acid reaction. A saturated solution of bromine water is added in considerable excess, and the liquid stirred vigorously for some time. The precipitate which separates is flocculent when first formed, but becomes more viscous after stirring, and adheres for the most part to the sides of the beaker, which, with its contents, is allowed to stand for about half an hour, or until all the precipitate is settled. The supernatant liquor is decanted through an asbestos filter. The precipitate adhering to the beaker is washed several times with cold distilled water, and the washings poured through the filter. Occasionally, when most of the free bromine is washed out of the precipitate, the liquid does not filter clear. It is therefore advisable to keep the washings separated from the filtrate, and, if necessary, wash with sodium-sulphate solution or with bromine water. The nitrogen in the precipitate is determined by the Gunning-Kjeldahl process as follows:—

The precipitate which has been collected on the asbestos filter, together with the asbestos, is returned to the beaker in which the precipitation took place; 20 c.c. of strong sulphuric acid are added, the beaker covered with a watch-glass and placed on a wire gauze over a lamp. When frothing has ceased, about 10 grms. of powdered potassium sulphate are added and the liquid boiled until colourless. After cooling, it is distilled with water, and the ammonia distilled off and determined in the usual way. The percentage of nitrogen found, when multiplied by the factor 6·33, or in the case of gelatin by 5·5, gives the amount of proteid matter precipitated by bromine. In the commercial gelatin above mentioned the nitrogen content was found to be 14·1 and 14 per cent, respectively, on two determinations. Solutions of creatinin, asparagin, and aspartic acid were found to yield no precipitates with bromine, but bromine was found to precipitate all albumen, acid albumen, and all peptones formed by the digestion of albumen with pepsin.

Application to Commercial Meat Extracts.

On applying the bromine method to commercial meat extracts the following results were obtained. The solutions of the Bovril preparations were not previously filtered, and therefore the figures contain the nitrogen and the fibre present.

Substance.	Nitrogen in precipitate by bromine.	Proteids (N×6·25).
Liebig Company's extract	1·41 per cent.	8·92 per cent.
Seasoned bovril	1·94 „	12·28 „
Bovril for invalids	2·64 „	16·71 „

Kœnig and Bœmer have shown that the proteid nitrogen in meat extracts is generally much over-estimated. They found a total of 1·17 per cent of proteid nitrogen in the Liebig Company's extract, which is equivalent to 7·41 per cent of total proteids, mostly albumose. The fact that bromine completely precipitates all proteid and gelatinoid matters in solution, affords a convenient means of solving certain problems which have hitherto presented considerable difficulty. For instance, in a solution which has been subjected to digestion it may be possible to precipitate all the unchanged proteids by saturation with zinc sulphate. The peptones which have been formed during digestion remain in solution and can be separated by filtration. In the filtrate the peptones can be completely precipitated by bromine, and thus the total quantity of these bodies formed during digestion can be accurately determined.

Allen and Searle applied this method to an examination of the Liebig Company's extract, 5 grms. of which were dissolved in 100 c.c. of water and the solution saturated with zinc sulphate. After filtering, bromine water was added to the filtrate and a precipitate produced which redissolved on diluting with water and the addition of hydrochloric acid. When the filtrate from the saturated zinc sulphate was previously diluted with water and acidulated, no precipitate was formed on the addition of bromine. This reaction shows that no considerable quantities of real peptones exist in Liebig's extract.

Since this bulletin was prepared for the press, an extensive article on the halogen derivatives of albumen has been published by F. Blum and W. Vaubel of Frankfurt, Germany ("Ueber Halogeneiweissderivate," *Journ. für Praktische Chemie*, 1897, lxvi., 393—6, and 1898, lvii., 365—396).

THE ESTIMATION OF IRON IN THE FERRIC STATE BY REDUCTION WITH SODIUM THIOSULPHATE AND TITRATION WITH IODINE.*

By JOHN T. NORTON, Jun.

The action of sodium thiosulphate on ferric iron has long been known, and depends upon the following reaction:—

$$2FeCl_3+2Na_2S_2O_3=2FeCl_2+Na_2S_4O_6+2NaCl.$$

As early as 1859, Sherer (*Gelehrte Anzeigen der König. Bayrisch. Acad.* vom Aug. 31, 1859) proposed a method for the estimation of ferric iron depending on the above reaction. Sherer's method of procedure was to act upon a solution of ferric chloride with sodium thiosulphate until the purple colour produced by the interaction of these two salts just vanished. Mohr's (*Anal. d. Chem. u. Pharm.*, cxiii., 260) experimental tests of this process were not successful. A year or two later, Kremer and Landolt (*Zeit. Anal. Chem.*, i., 214), after a careful investigation of Sherer's process, recommended it with the modification that any free hydrochloric acid present should be neutralised by sodium acetate until the solution assumed a red colour, just enough hydrochloric acid added to destroy this red colour, and sodium thiosulphate run into the solution in slight excess. When the liquid became perfectly colourless and gave no reaction for ferric iron with potassium sulphocyanide, the excess of sodium thiosulphate was titrated back with iodine and starch. The authors also state that the ferric iron should not be present in concentrated solution. Very good results were claimed for this process, but it apparently gained but slight recognition.

Oudemanns (*Zeit. Anal. Chem.*, vi., 129), who was the next to study the action of ferric iron and sodium thiosulphate, claimed that the addition of a small quantity of cupric salt to the iron solution hastened the reducing action of the sodium thiosulphate. Mohr ("Titrirmethode"), however, condemned this method also as unreliable, both because the sodium thiosulphate acted upon the copper as well as the iron and also because the potassium sulphocyanide, added as an indicator of the completeness of the reduction, produced a precipitate of cupric sulphocyanide which interfered with the reaction. In a second paper, Oudemanns (*Zeit. Anal. Chem.*, ix., 362) reiterated his former statement as to the accuracy of his method, but advised the use of a smaller quantity of the cupric salt. An improvement on Oudemanns's process was proposed by Haswell (*Repertorium der Analytischen Chem.*, i., 179), who mixed the moderately acid solution

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, viii., July, 1899.

of ferric chloride in the presence of a cupric salt with a few drops of sodium salicylate and then reduced with sodium thiosulphate previously standardised upon a known quantity of iron by the same process, and estimated the excess by potassium dichromate. Bruel (*Comptes Rendus*, xcvii., 954) modified this process by operating without the copper solution, relying merely on the discharge of the violet colour in a boiling solution by sodium thiosulphate standardised on a ferric solution of known strength.

Although considerable work has been done on the reaction between ferric iron and sodium thiosulphate, no process depending upon this reaction has obtained acceptance. In view, therefore, of previous work on the action of hydrochloric acid upon sodium thiosulphate (*American Journal of Science*, vii., 287; Chem. News, lxxx., p. 27), and with the idea that a careful control of the dilution and quantity of acid present might greatly better the accuracy of the method, it has seemed to me to be desirable to study this process again in detail.

The ferric oxide employed in the experiments was prepared with great care by the ignition of ferrous oxalate obtained by acting with oxalic acid on pure ammonium ferrous sulphate. To ascertain, however, if this oxide contained any impurity, about 0·5 of a grm. was put into a porcelain boat and submitted to the action of a current of hydrochloric acid gas and chlorine at a temperature of about 280° C.—according to a process recently described from this laboratory (Gooch and Havens, *Am. Journ. Sci.*)—until all the ferric salt is volatilised in the form of ferric chloride. A residue of 0·0010 grm. for every 0·5 of a grm. of the oxide was found, and this correction, small for the amounts generally used, has been applied in the following determinations. The sodium thiosulphate used was taken in nearly *n*/10 solution, and was standardised against an approximately decinormal solution of iodine which had been determined by comparison with decinormal arsenious acid made from carefully re-sublimed arsenious oxide.

In those experiments which deal with amounts of ferric oxide not exceeding 0·2 of a grm., measured portions of a solution of ferric chloride made of known strength by dissolving about 2 grms. of the pure carefully weighed ferric oxide in 20 c.m.³ of strong hydrochloric acid and diluting to 1 litre, were drawn from a burette. In the case of the larger quantities of ferric oxide the salt was weighed out, dissolved in hydrochloric acid, and brought to the required dilution. The ferric chloride, either drawn from the burette or prepared directly from the weighed oxide, was diluted with water, a drop of potassium sulphocyanide added to serve as an indicator, and an excess of sodium thiosulphate was run in until, after standing for a few minutes, the solution became perfectly colourless, and the excess of sodium thiosulphate was then titrated back with decinormal iodine after the addition of starch.

Several sources of error are plainly possible in the process: incompleteness in the reduction of the ferric salt; decomposition of the thiosulphate by the acid, resulting in the subsequent over-run of iodine; the possible tendency of the ferric salt under concentration to oxidise the thiosulphate to the condition of the sulphate rather than to that of the tetrathionate; and, finally, the oxidising action of the air, which may tend to keep up progressive oxidation of the iron salt and excessive expenditures of thiosulphate. The first three sources of difficulty tend to produce errors of deficiency; the fourth an error of excess.

The first step in the experimental study of the process was to determine the effect of varying dilution upon the estimation of a given quantity of iron reduced by sodium thiosulphate, taken in practically uniform excess above the amount theoretically required, in the presence of 1 c.m.³ of hydrochloric acid.

This table shows plainly that with quantities of ferric oxide present up to 0·1 grm. the dilution can vary from 400 c.m.³ to 1000 c.m.³ for each c.m.³ of strong hydrochloric acid and still give excellent results. At a dilution greater than 1000 c.m.³ the action of the thiosulphate is evidently incomplete, and at a smaller dilution than 400 c.m.³ the decomposing action of the acid on the thiosulphate becomes noticeable. When larger quantities of iron oxide are dealt with, it appears that the dilution ought to be increased proportionally with the quantity of ferric oxide present as well as with that of the acid. This is illustrated in Experiments 9—15 of the table. On this account it seems necessary, assuming that the quantity of acid present is always kept within the maximum strength mentioned (1 c.m.³ to 400 c.m.³), to regulate the dilution from the approximate quantity of the iron so that not less than 400 c.m.³ of water shall be used to every 0·1 grm. of iron oxide present. Under properly regulated conditions of dilution as regards acid and the iron salt, the reduction is completed in from five to ten minutes.

Table I.

	Fe_2O_3 taken.	Fe_2O_3 corrected.	Dilution.	HCl.	$Na_2S_2O_3$ in excess.	Fe_2O_3 found.	Error.
	Grm.	Grm.	C.m.³.	C.m.³.	C.m.³.	Grm.	Grm.
1.	0·1000	0·0998	100	1	18·08	0·0957	0·0041 −
2.	0·1000	0·0998	200	1	20	0·0966	0·0032 −
3.	0·1000	0·0998	300	1	17·56	0·0995	0·0003 −
4.	0·1000	0·0998	400	1	17·16	0·0998	0·0000
5.	0·1000	0·0998	600	1	17·76	0·0996	0·0002 −
6.	0·1000	0·0998	800	1	17·65	0·0993	0·0005 −
7.	0·1000	0·0998	1000	1	18·02	0·0988	0·0010 −
8.	0·1000	0·0998	1200	1	17·95	0·0977	0·0021 −
9.	0·1000	0·0998	1400	1	17·99	0·0965	0·0033 −
10.	0·1000	0·0998	1600	1	18·01	0·0947	0·0051 −
11.	0·2001	0·1997	400	2	27·05	0·2029	0·0032 +
12.	0·2001	0·1997	800	2	15·95	0·1998	0·0001 +
13.	0·4998	0·4988	1000	2	22·36	0·5104	0·0126 +
14.	0·5051	0·5041	1800	4	15·27	0·5026	0·0017 −
15.	0·4002	0·3994	1500	4	27·29	0·3996	0·0002 +
16.	0·7502	0·7487	1000	1	9·73	0·7572	0·0085 +
17.	0·7029	0·7015	2000	4	12·67	0·7004	0·0011 −

Great excesses of acid, however, contrary to the statement of Kremer (*Zeit. Anal. Chem.*, i., 214), retard the reduction greatly, and, in spite of the tendency of the thiosulphate to decomposition and the production of errors of deficiency under such circumstances, plus errors due to partial oxidation come to light. This fact appears in the following table, which records the results of processes lasting many hours.

Table II.

	Fe_2O_3 taken.	Fe_2O_3 corrected.	Dilution.	HCl.	$Na_2S_2O_3$ in excess.	Fe_2O_3 found.	Error.
	Grm.	Grm.	C.m.³.	C.m.³.	C.m.³.	Grm.	Grm.
18.	0·5012	0·5002	1700	10	25·99	0·5308	0·0306 +
19.	0·7512	0·7497	1200	15	57·8	0·7685	0·0188 +
20.	0·7520	0·7505	2000	15	56·4	0·7983	0·0478 +
21.	0·7520	0·7505	1700	15	27·2	0·7627	0·0122 +

As to the temperature at which the reduction should be made, my experience, contrary to that of Kremer, goes to show that no elevation above atmospheric conditions is necessary; under the conditions of acidity and dilution laid down, the process of reduction is complete within ten minutes after the introduction of the thiosulphate; moreover, former experience (*Am. Journ. Sci.*, vii., 287) shows clearly the danger of submitting mixtures of sodium thiosulphate and acid to temperatures much above the ordinary. On the other hand, artificial reduction of temperature tends to retard the action to an impossible degree. Thus, in an experiment it took five minutes to reduce 0·0500 of ferric oxide at 21° C. completely at a dilution of 200 c.m.³ and in the presence of ½ c.m.³ of hydrochloric acid; under conditions otherwise precisely similar, excepting that the temperature was lowered to 0° C., the action lingered forty-five minntes.

Lastly, the question as to the excess of thiosulphate

necessary to complete the reduction within a reasonable time must be considered. In nearly all previously recorded experiments the excess of thiosulphate was not less than 15 c.m.³ of the *n*/10 solution. The following table shows the effect of diminishing this excess.

TABLE III.

	Fe_2O_3 taken.	Fe_2O_3 corrected.	Dilution.	HCl.	$Na_2S_2O_3$ in excess.	Fe_2O_3 found.	Error.
	Grm.	Grm.	C.m.³.	C.m.³.	C.m.³.	Grm.	Grm.
22.	0·0250	0·0250	400	½	12·2	0·0241	0·0009 −
23.	0·0500	0·0499	400	½	12·2	0·0495	0·0004 −
24.	0·0500	0·0499	400	½	13·66	0·0493	0·0006 −
25.	0·1000	0·0998	400	1	7·31	0·0984	0·0014 −
26.	0·1000	0·0998	400	1	7·63	0·0972	0·0026 −
27.	0·1001	0·0999	400	1	12·88	0·1007	0·0008 +
28.	0·1498	0·1495	600	1½	11·97	0·1475	0·0020 −
29.	0·1996	0·1992	800	2	12·43	0·1980	0·0012 −

From the above experiments, taken in connection with those of Table I., it is clear that there should always be present an excess of at least 15 c.m.³ of the *n*/10 solution of sodium thiosulphate. If the quantity of hydrochloric acid is kept very low there is no reason why this excess of thiosulphate could not be considerable without producing any disturbing effect. Practically, however, the presence of an excess between the limits of 15 c.m.³ and 35 c.m.³ of the *n*/10 solution has been found to give the most satisfactory results.

To recapitulate, then, it has been shown that the dilution must be at least 400 c.m.³ for each 0·1 of a grm. of iron oxide present, that the quantity of acid should never exceed 1 c.m.³ of the strong acid to each 400 c.m.³ of water, that the time of reduction must be short to avoid progressive oxidation, that the temperature of the solution should be kept at the normal temperature of the atmosphere, and finally that the excess of sodium thiosulphate present should never be less than 15 c.m.³ of the *n*/10 solution. In the case of large dilution the use of freshly-boiled water is recommended, so as to avoid the re-oxidising effect of the air upon the reduced iron. In the experiments included in the following table, the above precautions were closely adhered to and manifestly satisfactory results were obtained.

TABLE IV.

	Fe_2O_3 taken.	Fe_2O_3 corrected.	Dilution.	HCl.	Excess $Na_2S_2O_3$.	Fe_2O_3 found.	Error.
	Grm.	Grm.	C.m.³.	C.m.³.	C.m.³.	Grm.	Grm.
30.	0·0125	0·0125	200	⅛	23·5	0·0125	0·0000
31.	0·0250	0·0250	400	¼	21·98	0·0250	0·0000
32.	0·0250	0·0250	400	¼	17·	0·0250	0·0000
33.	0·0250	0·0250	400	¼	17·	0·0250	0·0000
34.	0·0500	0·0499	400	½	24·	0·0498	0·0001 −
35.	0·0500	0·0499	400	½	19·	0·0498	0·0001 −
36.	0·0500	0·0499	400	½	15·1	0·0497	0·0002 −
37.	0·0500	0·0499	400	½	19·	0·0498	0·0001 −
38.	0·1001	0·0999	400	1	23·1	0·0993	0·0006 −
39.	0·1001	0·0999	400	1	17·93	0·0997	0·0002 −
40.	0·1001	0·0999	400	1	22·92	0·0997	0·0002 −
41.	0·1001	0·0999	400	1	18·	0·0997	0·0002 −
42.	0·1001	0·0999	400	1	16·	0·0996	0·0003 −
43.	0·1498	0·1495	600	1½	23·26	0·1493	0·0002 −
44.	0·1498	0·1495	600	1½	16·66	0·1493	0·0002 −
45.	0·1498	0·1495	600	1½	26·87	0·1475	0·0020 −
46.	0·1996	0·1992	800	2	22·38	0·1990	0·0002 −
47.	0·1996	0·1992	800	2	17·29	0·1999	0·0007 +
48.	0·1996	0·1992	800	2	22·20	0·1991	0·0001 −
49.	0·4045	0·4037	1600	4	16·03	0·4042	0·0005 +
50.	0·4045	0·4037	1600	4	16·2	0·4023	0·0014 −
51.	0·4018	0·4010	1600	4	16·34	0·4007	0·0003 −
52.	0·5051	0·5041	1800	4	15·27	0·5026	0·0015 −

As seen in the table, this process is very accurate—especially in the use of small amounts of ferric oxide. The introduction of cupric sulphate, as recommended by Oudemanns, or of sodium salicylate according to Haswell's method, seems to be unnecessary and only complicates the process.

In treating ferric oxide, the following method of procedure is recommended:—Dissolve an amount not exceeding 0·2 grm. of the oxide in hydrochloric acid, evaporate to a pasty mass, dilute to about 800 c.m.³ with freshly-boiled water, add a drop of potassium sulphocyanide, and into this solution run 50 c.m.³ of approximately *n*/10 sodium thiosulphate; allow the liquid to stand until perfectly colourless, and determine the excess of thiosulphate by *n*/10 iodine and starch. For quantities of iron oxide up to 0·2 of a grm. this process is quick and most accurate; when care is taken to preserve the relations of acidity and dilution, twice the amount of ferric oxide mentioned above may be handled.

In conclusion, I wish to thank Prof. F. A. Gooch for his kind advice and many suggestions.

THE TITRATION OF OXALIC ACID BY POTASSIUM PERMANGATATE IN PRESENCE OF HYDROCHLORIC ACID.*

By F. A. GOOCH and C. A. PETERS.

(Concluded from p. 80).

As Kessler has noted, a sufficiency of the manganous salt, acting no doubt as the medium of transfer of oxygen, may bring about interaction between the permanganate and the oxalic acid at atmospheric temperatures without the tedious delay ordinarily encountered in the attempt to consummate that action in cold solutions. It would seem natural that the manganic hydroxide formed in the Guyard reaction at low temperatures should yield more readily to the reducing action of the oxalic acid than the more anhydrous form to be expected in hot solutions, so that at such temperatures the limits as to proportions of manganous salt, acid, and dilution, within which favourable action may take place, should be wider; moreover, the undesirable action of the permanganate upon hydrochloric acid, when that acid is present, should be less appreciable at lower temperatures. In our experiments, therefore, upon the oxidation of oxalic acid by potassium permanganate in presence of hydrochloric acid, we have studied the effect of varying the proportions of the manganous salt both at atmospheric temperatures and the higher temperatures generally employed.

From these results (Table IV.) it appears that the presence of a suitable amount of manganous salt—either the sulphate (Experiments 4—7, 13—15, 22—24) or the chloride (Experiments 10—12, 16—20)—is capable, either in cold solution (Experiments 1—20) or in hot solution (Experiments 22—24) of preventing the action of the permanganate upon the hydrochloric acid. It appears, also, that, for a given dilution and strength of acid, less manganous salt is needed in the cold solution (Experiments 4—7) than in the hot solutions (Experiments 22—24). Thus, in the hot solution, at a dilution of 145 c.m.³ to 500 c.m.³, 1 grm. of manganous sulphate must be present with 5 c.m.³ of strong hydrochloric acid, with or without sulphuric acid; while in the cold solution 0·04 grm. of either the sulphate or chloride is enough to secure adequate protective effect. Experience showed, however, that 0·5 grm. or 1·0 grm. of the manganous salt should be present in order to push the reaction with reasonable speed in cold solutions.

Wagner (*loc. cit.*) has made record of the increased evolution of chlorine in oxidations of ferrous chloride by potassium permanganate in presence of various salts, of which barium chloride was the most active. We have made some experiments, therefore, to determine whether

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. vii., June, 1899.

TABLE IV.

(Temperature 20—26° C.).

Number of experiment.	Volume at beginning of titration.	H_2SO_4. 1 : 1.	HCl. Sp. gr. 1·09.	Ammonium oxalate. 1/10 N.	$KMnO_4$.	$MnSO_4 5H_2O$.	$MnCl_2.4H_2O$.	Variation from standard.
	C.m.³.	C.m.³.	C.m.³.	C.m.³.	C.m.³.	Grms.	Grms.	C.m.³.
1.	130	—	10	25	23·90	0·0040	—	+0·15
2.	130	—	10	25	23·90	0·0120	—	+0·15
3.	130	—	10	25	23·80	0·0250	—	+0·05
4.	130	—	10	25	23·75	0·0400	—	+0·00
5.	130	—	10	25	23·76	0·0500	—	+0·01
6.	130	—	10	25	23·70	0·1000	—	−0·05
7.	130	—	10	25	23·75	0·2000	—	0·00
8.	130	—	10	25	24·20	—	0·0200	+0·45
9.	130	—	10	25	23·95	—	0·0200	+0·20
10.	130	—	10	25	23·80	—	0·0400	+0·05
11.	130	—	20	25	23·75	—	0·0400	0·00
12.	130	—	30	25	23·75	—	0·0400	0·00
13.	130	—	10	25	23·75	1·0000	—	0·00
14.	130	—	10	25	23·75	2·0000	—	0·00
15.	130	—	10	25	23·75	3·0000	—	0·00
16.	130	1	—	25	23·72	—	1·0000	−0·03
17.	130	1	—	25	23·74	—	2·0000	−0·01
18.	130	1	—	25	23·72	—	3·0000	−0·03
19.	130	2	—	25	23·70	—	0·5000	−0·05
20.	130	3	—	25	23·75	—	0·5000	0·00
				(Temperature about 80°).				
21.	145	10	10	25	23·90	0·5000	—	+0·15
22.	145	10	10	25	23·70	1·0000	—	−0·05
23.	500	10	10	25	23·75	1·0000	—	0·00
24.	500	—	10	25	23·70	1·0000	—	−0·05
25.	500	—	10	25	24·10	0·5000	—	+0·35

TABLE V.

(Volume at beginning of titration = 140 c.m.³. Temperature = 20—24° C.).

Ammonium oxalate.	HCl. Strongest.	$MnCl_2.4H_2O$.	$BaCl_2$.	$SrCl_2$.	$CaCl_2$.	$MgCl_2$.	$KMnO_4$ used.	Error.
C.m.³.	C.m.³.		Grms.	Grms.	Grms.	Grms.	C.m.³.	C.m.³.
25	5	0·5	—	—	—	—	26·05	0·00
25	5	—	—	—	—	—	27·45	+1·40
25	5	—	2	—	—	—	26·50	+0·45
25	5	—	—	2	—	—	26·53	+0·48
25	5	—	—	—	2	—	26·36	+0·35
25	5	—	—	—	—	2	26·13	+0·08
25	5	0·5	2	—	—	—	26·05	0·00
25	5	0·5	—	2	—	—	26·10	+0·05
25	5	0·5	—	—	2	—	26·10	+0·05
25	5	0·5	—	—	—	2	26·05	0·00
25	10	1·0	2	—	—	—	26·10	+0·05
25	10	1·0	—	2	—	—	26·05	0·00
25	10	1·0	—	—	2	—	26·06	+0·01
25	10	1·0	—	—	—	2	26·11	+0·06

such action would appear in the oxidation of oxalic acid in cold solutions containing certain salts, and, if so, whether it would be preventable by the presence of the manganous salt under our conditions of working. From the results given in Table V., it is plain that the evolution of chlorine in cold solutions is less in the presence of these salts than when hydrochloric acid is used without them, and that such evolution may be entirely prevented (within the proportions of our work) by the presence of 0·5 grm. to 1 grm. of manganous chloride.

Finally, it appears as the result of an investigation, that the titration of oxalic acid by potassium permanganate in presence of hydrochloric acid is ordinarily attended with some inaccuracy due to liberation of chlorine from the hydrochloric acid; that this tendency may be overcome by the presence of a manganous salt (either the sulphate or chloride); that 1 grm. of the manganous salt is enough to so affect the conditions of equilibrium that titrations in moderate volumes (100 c.m.³ to 500 c.m.³) and in presence of hydrochloric acid (5 c.m.³ to 15 c.m.³ of the strong acid) may be conducted with safety and reasonable rapidity, either with or without sulphuric acid, at the ordinary atmospheric temperature.

ON THE

CLAIMS OF DAVYUM TO RECOGNITION AS A CHEMICAL ELEMENT.*

By J. W. MALLET.

(Concluded from p. 81).

THE crude common salt in rose-coloured crystals dissolved almost completely in water, producing a solution of rather orange or aurora-red colour, having a distinct,

* From the *American Chemical Journal*, Vol. xx., No. 9.

though not very strong, acid reaction to litmus. Using a minimum quantity of cold water, applied in several successive portions, a minute residue was left undissolved, but a few m.grms. from a couple of hundred grms. of the salt, which residue consisted partly of fine light grey matter resembling that already noticed, but chiefly of a buff-coloured powder, appearing under the microscope (with a power of 250—450 diameters) as distinctly transparent and crystalline, with the general aspect of minute octahedra and cubo-octahedra; no colours shown in polarised light. The clear aqueous solution was reduced by a rod of extremely pure zinc and a little hydrochloric acid. Most of the metallic precipitate thrown down was loose and flocculent, but there was a strong tendency to the formation of a *specular* and pretty firmly adherent deposit on the glass of the beaker and stirring-rod. The precipitate, dried at 120° C., represented a little less than 0·2 per cent of the crude salt taken. This precipitate, which if strongly ignited in the air gave off a slight but unmistakable odour of osmium tetroxide, was re-dissolved by *aqua regia*, and the solution was mixed with a moderate excess of sodium chloride, evaporated almost to dryness, re-diluted with water, and again evaporated to remove surplus acid, and finally allowed to stand in the cold for two or three days, the concentration being such that only a little sodium chloride separated out. On decanting, and cautiously removing by water the small remaining surplus of sodium chloride, a little more of a buff-coloured residue was obtained, looking, both to the naked eye and under the microscope, like the original residue from the treatment of the crude rose-coloured salt with water. The buff-coloured material from these two sources—that first obtained having been freed from the light grey powder by washing with a saturated solution of common salt, and decantation—was washed with alcohol, in which it seemed to be practically insoluble, and dried. A little specimen of it dissolved in a large quantity of water. Another small portion, tested spectroscopically, showed the presence of sodium with a trace of potassium. The principal part was dried at 120° C., weighed, and heated to redness in a stream of hydrogen; the residual metal, washed free of alkaline chloride, was dried and weighed; it formed 37·1 per cent of the salt decomposed. Assuming this double chloride to be anhydrous, sodium to be the only alkaline metal present, and a single metal of the platinum group to be associated with it, the atomic mass of such platinum metal would be 151·5 for the formula Na_2MCl_6, or 165 for the formula Na_3MCl_6. Of these formulæ the former is the more probable, and leads to an approximate value for the atomic mass not very different from that assigned by Kern to davyum. Both determinations were made with quantities altogether too small for any very accurate result.

The general properties of the metallic material thus obtained agreed in the main with those described by Kern, as far as they could be compared by experiments on so minute a scale, and after solution in *aqua regia*, which was effected but slowly and with difficulty, the reactions in the liquid way were pretty nearly such as he obtained. But, although a small part of the solution gave a red colouration with potassium thiocyanate, a reaction pointed out by Kern as among those particularly characteristic of davyum, a simple additional test with potassium ferrocyanide at once showed the presence of iron, though in small amount, thus accounting for the red colour. Furthermore, on placing, in the chief portion of the solution, a little lump of sal ammoniac and allowing it to remain until it had dissolved to saturation, a dark brown-red precipitate was formed, from which the ordinary reactions of iridium were obtained, while the remaining liquor, evaporated to dryness and the solid residue ignited, left rhodium, probably not pure, but identifiable by the action upon it of fused potassium acid sulphate; so that the material examined consisted, not of a single distinct metal, but merely of a mixture of iridium and rhodium with a little iron. The whole quantity available was quite insufficient for any exact quantitative analysis, but the very rough approximation to a mean atomic mass indicates that the two metals of the platinum group must have been present in not very unequal quantities.

Of course the results thus obtained, while lending no support to a belief that there is such an element as davyum, do not suffice to disprove its existence. It may, however, be remarked that in the account given by Kern himself of his experiments, there are some points tending to increase doubt as to the conclusion which he reached. Thus there is, probably from carelessness, some erroneous statement of facts, as, for instance, the assertion that *like platinum chloride* the chloride of davyum forms double salts with ammonium and potassium chlorides *insoluble in water and easily soluble in absolute alcohol.* It is suggestive that davyum is said to have been obtained from native platinum in the separation of rhodium and iridium. There is no allusion to the well-known fact of the reactions afforded by one of the platinum metals being modified by the presence along with it of others of this group, notably true of iridium solutions when containing also platinum, palladium, or rhodium. It is unsatisfactory to find the statements that "careful qualitative analyses showed no presence whatever of iron," and that the author's davyum "was found to contain no metals of other groups" without any details being given of the tests by which it was supposed that these points were established.

On the whole it seems most probable that, in default of better proof of elementary character than has yet been given, davyum is to be looked upon as merely a mixture of iridium and rhodium with a little iron; and, hence, that we have not yet reason to believe in the existence of a third triad group of platinum metals.

SEVENTEENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its Seventeenth Annual Report, covering the twelve months ending August, 1899.

Works Published.

"A Select Bibliography of Chemistry, 1492—1897." By Henry Carrington Bolton. First Supplement. Smithsonian Miscellaneous Collections 1170. City of Washington, 1899. Pp. x.+489. 8vo.

This work includes titles omitted in the volume published in 1893, and brings the literature down to 1897, the plan and scope being the same. In collecting the 5554 titles the author had the co-operation of eminent men of science and letters in several parts of the world.

"Index to the Literature of Thallium, 1861—1897." By Miss Martha Doan.

This is passing through the press, and will probably be issued before this Report is presented to the Section. It will form one number of the Smithsonian Miscellaneous Collections.

Works in Preparation and Reports of Progress.

"Index to the Literature of Zirconium." By A. C. Langmuir and Charles Baskerville.

The manuscript has been critically examined by each member of the Committee and unanimously recommended to the Smithsonian Institution for publication.

"A Select Bibliography of Chemistry, 1492—1897." Second Supplement. By Henry Carrington Bolton.

* Advance proofs from the *Proceedings of the American Association for the Advancement of Science*, Columbus Meeting, 1899.

The manuscript of this work, which embraces Chemical Dissertations only, has been completed and presented to the Smithsonian Institution.

"A Bibliography of Malonic Acid and its Derivatives" has been begun by Dr. Thomas Clarke, University of North Carolina.

A Third Supplement to the "Select Bibliography of Chemistry" has been commenced by Dr. H. Carrington Bolton.

"Science Abstracts." The Physical Society of London published in 1895—1897 three volumes of "Abstracts of Physical Papers from Foreign Sources," edited by Mr. J. Swinburn. Each volume has author and subject indexes. Since January, 1898, these abstracts have appeared monthly in enlarged scope under the title "Science Abstracts: Physics and Electrical Engineering." Issued under direction of the Institution of Electrical Engineering and the Physical Society of London. J. Swinburn, Editor. Monthly. Spon and Chamberlain, Agents, New York.

This important undertaking includes electrochemistry and chemical physics. The editor is assisted in his work by W. R. Cooper and a corps of fifty-two abstractors.

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OBITUARY.

PROF. ROBERT WILHELM BUNSEN.

IT is with sincere regret that we have this week to record the death of another of the most distinguished chemists of the century, in the person of Professor Bunsen, who died at Heidelberg on the 16th of this month, at the ripe age of 88.

Prof. Bunsen was born on the 13th March, 1811, at Göttingen, where his father was Professor of Occidental Literature. He studied Science at that University, and after continuing his education at Paris, Berlin, and Vienna, he took his degree in 1833. In 1836 he succeeded Wöhler as Professor of Chemistry in the Polytechnic Institution at Cassel, and in 1838 was appointed Assistant-Professor in the University of Marburg. Three years later he was made Titular Professor, and then became Director of the Chemical Institute; he also held several other appointments.

His great work dates back to 1856, when he shared with Professor Kirchhoff the discovery of spectroscopic astronomy, on which our knowledge of the chemical constituents of the sun and stars has been built up. It is widely thought that the chief merit for the discovery of spectrum analysis should be awarded to Bunsen. Amongst his numerous other discoveries we may mention the battery and burner which bear his name. He was also the author of many scientific works, and had received several honorary degrees from Universities throughout Europe. In 1833 he was appointed one of the eight Foreign Associates of the Paris Academy of Sciences.

We take the following from a notice of Professor Bunsen which appeared in *The Times* of the 17th inst.:—

Full of years—he was born in 1811—and full of honours, he has passed to his rest after a long life exclusively devoted to the prosecution of his science. The latter years of his life were passed in retirement at Heidelberg. He retained his faculties to the end of his days, and even in his 88th year, though his hearing was somewhat impaired, the chief complaint he had to make to an English visitor was that he was beginning to find that his eyesight was not so good as it used to be. With his death the last link is severed between the great German scientists of the past and their followers of to-day, who endeavour—with what success may be a matter of opinion—to walk in the footsteps of their scientific forbears. To each of these, all the world over, the death of Bunsen comes as a personal grief. For none, not even Liebig or Hofmann, have left behind them such warm and affectionate memories as those which cluster round the name of the great investigator and teacher whose hand and voice are now stilled.

The son of a distinguished Göttingen theologian, Bunsen was brought up from his earliest days in a University atmosphere, and soon showed that power of keen observation and manipulative dexterity which placed him for long years in the forefront of modern experimental philosophers. The facts of his life may be shortly stated. Born in 1811, he graduated at Göttingen University as Ph.D. in 1831. After spending a few years in study at Paris, Berlin, and Vienna, in 1836 he succeeded Wöhler as Professor of Chemistry in the Polytechnic School at Cassel. Two years later he went to Marburg; then, in 1852, after a short interval at Breslau, he was appointed to the chair of experimental chemistry at Heidelberg, where he remained, in spite of a tempting invitation to Berlin University, until his resignation in 1889. Many academical distinctions of course fell to his share, both in his own country and abroad. In England the Royal Society—which in 1858 elected him one of its foreign members—awarded him the Copley medal in 1860, and seventeen years afterwards chose him and his fellow-worker Kirchhoff to be jointly the first recipients of the newly-instituted Davy medal.

As a "privat docent" in his native University, he first showed his ability in the prosecution of a difficult and dangerous investigation upon a series of poisonous and explosive organic compounds of arsenic, and in the course of these experiments he met with an accident which nearly cost him his life, but, undaunted, he pursued his work until he succeeded in placing the chemistry of the whole subject in a clear light. To enumerate the discoveries in almost every branch of chemistry made by his unwearied assiduity would fill a treatise. Suffice it here to enumerate those which have made Bunsen's name a household word. First came the Bunsen voltaic-battery, which, supplanting the more expensive form bearing the name of our countryman Grove, was generally used as the cheapest and most effective mode of generating electricity until the dynamo displaced all forms of chemical batteries. Next came the Bunsen gas burner, which, it is not too much to say, is now not only a necessity in the laboratory, but in every household and every manufactory where a clean flame is wanted. About his discovery of this simple and effective apparatus an interesting tale could be told. No one before Bunsen had thought it possible that a mixture of coal-gas and air could be made to burn without explosion from a simple tube-burner. His clear conception of the laws which apply to the inflammation of such a mixture showed him that it was possible to arrange the dimensions in such a way that a steady, smokeless, and highly combustible mixture could be obtained, but a long series of delicate experiments was needed before the perfect burner which now bears his name resulted. Of other investigations carried out by Bunsen may be mentioned those on the chemistry of blast-furnace gases, in conjunction with the late Lord Playfair, on actinometry and the chemical action of light with Sir Henry Roscoe, and on the geological conditions of Iceland and the theory of the geysers—the result of a visit to that island in 1847.

The research, however, by which, perhaps, more than

any other the name of Bunsen will go down to posterity, linked with that of his colleague Kirchhoff, is the discovery of spectrum analysis, for this opened out a field of experiment so new and so vast that it may well be said to be the most important scientific result accomplished during the latter half of the century, a time pregnant with work of a truly marvellous character. To have added a new branch to Chemical Science which throws a clear and wholly unexpected light upon the constitution of terrestrial matter, which has been the means of discovering many new chemical elements, and of proving the widespread distribution of others hitherto considered as rare, would in itself have been a work of primary significance; but when to that is added the fact that by means of this far-reaching method the bounds of our planet are outstepped and a knowledge not only of the chemical composition of the sun and of the far-distant stars, but even of their rates of motion, have thus been obtained, an idea may be formed of the debt of gratitude which all interested in human progress must feel to the two great twin brethren who in their quiet laboratory at Heidelberg revealed such hidden secrets. But these, though the best-known and most popular of the achievements of the Heidelberg master, are not more important from a scientific point of view than many others all known and valued by the chemist and physicist. To have first instituted methods of almost astronomical precision in the measurement and separation of gases, and thus to have laid on a firm foundation the branch science of gas analysis, is in itself sufficient to have marked him as one of the first experimentalists of the age. Add to that his numerous memoirs on purely chemical subjects, all marked by the same accurate work: add again his researches in physical chemistry; on the measurement of the chemical action of light—carried on in conjunction with one of his pupils—and, again, one on a new and improved method of determining specific heat, not forgetting his chemico-geological researches which constitute what may well be termed an epoch-making discovery as to the composition of the volcanic rocks of our planet,—and it is not too much to say that for variety and importance the theoretical and experimental work proceeding from his brain and hands has rarely, if ever, been exceeded.

This work, although great, is by no means the only, or even the greatest, work achieved by Bunsen. He has built up a vast and enduring reputation by his labours as a teacher and as a master craftsman. Passionately devoted to his laboratory and to his students, he formed a school of chemistry second only—and about that there may be a question—to that of Liebig at Giessen. His lectures were original and most instructive, but it was in the patient teaching in the laboratory that his genius showed itself strongest, and the pupils from all parts of the world who were fortunate enough to work under him in his most prolific days in Heidelberg all conceived for him the deepest feelings of respect and affection, his precept and example having influenced their whole lives. Those who had the privilege of intimate association with him knew him as the best and most reliable and most affectionate of friends. His presence was always welcomed in the academic circles of his University, for his simple and original nature—disliking show and despising pretence—exhibited in such society a fund of quiet humour which gave a special zest to his presence and conversation. Amongst his academic colleagues no one was honoured as he. Orders and decorations from all parts were his by the score; but these he valued less than the recognition by his brother men of science of the work he had done as typified by election as member of scientific societies, and amongst these he always placed in front rank that of the foreign Fellowship of our Royal Society.

Sodium Persulphate as a Germicide.—Friedlaender (*Pharm. Centralhalle*) reports favourably on the antiseptic and germicidal properties of sodium persulphate, $Na_2S_2O_8$.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 4, July 24, 1899.

Isomeric Forms of Chromic Acetate.—A. Recoura.—In a preceding paper the author announced that he had established the existence of four isomeric forms of chromic acetate, $Cr(C_2H_3O_2)_3$. The normal acetate is an ordinary metallic salt, of a lilac-grey colour, which dissolves in water, giving a yellowish-green solution. The salt is insoluble in acetic acid. The violet acetate is obtained in a solid state, by leaving a solution of the normal acetate to evaporate to dryness under a bell-jar over strong sulphuric acid and in presence of acetic acid. The salt appears in the form of thin, brilliant, violet plates. When exposed to the air, the substance slowly loses acetic acid.

Mixed Argento-cupric Basic Salts.—Paul Sabatier.—By direct contact of cupric hydrate with silver solutions, the author obtained mixed basic salts, which may be divided into two distinct classes.—(1) Tricupric, of which he obtained the nitrate and the sulphate; and (2) Bicupric, of which he obtained the nitrate, chlorate, and hyposulphate. Except in the case of the sulphate, where the very slight solubility of the silver salt hinders the reaction, these salts can be equally well obtained, under certain conditions, by the action of silver oxide on the cupric salts.

Purification of Iridium. — E. Leidie. — Instead of using the old dry method for the purification of iridium, the author suggests a method founded on the conversion of the metal into chloride and then treatment with sodium nitrite. The iron and lead are first precipitated as oxides, the gold in the form of the metal itself. There remains then double nitrites of ruthenium, rhodium, and iridium, and sodium osmiate. The ruthenium and osmium can be eliminated as volatile peroxides, whilst the rhodium and iridium are converted into the double chlorides with sodium chloride, in which compound the two metals are easily separated. The author proposes to generalise this method to the purification of all the metals of the platinum group.

A Double Nitrite of Ruthenium and Potassium.—L. Brizard.—The author has obtained a new double nitrite of ruthenium and potassium, differing from the two already known in properties and constitution. Analysis shows the formula to be $Ru_2H_2(NO_2)_4.3NO_2K.4H_2O$. The action of hydrochloric acid on this salt transforms it into the complex double chloride, which was the starting-point for the original preparation of the nitrite. The reaction, very slow in the cold, but becoming more rapid on boiling, may be represented by the equation—

$$Ru_2H_2(NO_2)_4.3NO_2K+8HCl=$$
$$=Ru_2H_2NO.Cl_3.3KCl.2HCl+2NO+4NO_2+3H_2O.$$

Some Opium Alkaloids.—Emile Leroy.—The author has determined the heats of combustion, hydration, formation, solution, and neutralisation, for the following opium alkaloids:—Codeine, morphine, thebaine, papaverine, and narcotine.

Dichlor-3, 4-Butanoic Acid.—R. Lespieau.—The two possible formulæ for this acid are:—

$CH_2.Cl.CH(OH)CH_2CN$ and $CH_2Cl.CH(CN)CH_2.OH$.

The author's experiments show the former to be the most probable formula.

Oxidation of Propylglycol by Bromine Water.—André Kling.—When a mixture of 1 molecule of propylglycol with 2 molecules of bromine dissolved in water are exposed to the rays of the sun, the mixture after a time

becomes decolourised, and it is found that the propylglycol is transformed partially into acetol according to the equation—

$$\begin{array}{l} CH_3 \\ | \\ CH.OHO \\ | \\ CH_2.OH \end{array} = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_2.OH. \end{array} + H_2O$$

Action of Bromine on Isobutyl Bromide in the presence of Anhydrous Aluminium Bromide and Aluminium Chloride. — A. Mouneyrat. — The author starts his series of experiments with monobromobutane, $CH_3CH(CH_3)CH_2Br$. This is acted upon by bromine in the presence of aluminium bromide. Four substances are obtained from this reaction: — (1) Isobutylene bromide; (2) A tribromoisobutane, boiling at 130° (pressure 26 m.m.; (3) Tetrabromisobutane; (4) A tribromoisobutane, boiling at 112°, and with the probable formula $CH_3.CBr(CH_3)CHBr_2$. This latter is obtained in considerable excess of the others.

MISCELLANEOUS.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1899, the Laboratory was attended by forty-eight Students. Of these, thirty-one were from Germany, three from Russia, two from England, two from Austria, and two from Holland, one from Switzerland, one from Belgium, one from France, one from Italy, one from Spain, one from Norway, one from Sweden, and one from the United States of America. There were three Assistants in the Instruction-Laboratory, and twenty-one in the Versuchsstationen (private laboratories). In the certified body of Teachers there has been no change. To this body belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Dr. med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and J. Huber (architect). The next Winter Term begins on October 16th. During the Summer Term, 1890, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) on behalf of manufacture, trade, mining, agriculture, and hygiene.

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Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896). Alfred Jörgensen, "Micro-Organisms and Fermentation," London (F. W. Lyon), 1893.

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ALFRED BLENKINSOP,
Secretary.

Truro, Cornwall,
August 18th, 1899.

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Lecturer—FRANCIS E. FRANCIS, B.Sc., Ph.D.
Demonstrator—D. H. JACKSON, M.A., B.Sc., Ph.D.

The SESSION 1899-1900 begins on October 3rd. Lectures on Inorganic, Organic, and Advanced Chemistry will be delivered during the Session. The Laboratories are fitted with the most recent improvements for the study of Practical Chemistry in all its branches. In the Evening the Laboratory is opened and Lectures on Inorganic Chemistry, at reduced fees, are delivered. Several Scholarships are tenable at the College.

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LECTURES.

Experimental Chemistry (Inorganic)	Prof. H. FRESENIUS, Ph.D.
Experimental Physics	Prof. W. FRESENIUS, Ph.D.
Stöchiometry	
Organic Chemistry	L. GRÜNHUT, Ph.D.
Chemical Technology	
Microscopy, with exercises in Microscopic work	W. LENZ, Ph.D.
Chemistry and Analysis of Foods ..	Prof. H. FRESENIUS, Ph.D. Prof. W. FRESENIUS, Ph.D., and Prof. E. HINTZ, Ph.D.
Hygiene	Dr. med. G. FRANK.
Practical exercises in Bacteriology ..	
Technical Drawing, with exercises ..	J. HUBER.

The next Session commences on the 16th of October. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to one of the Directors.

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(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

It cannot he denied that as the years roll on competition is getting more and more keen, and the choice of a profession requires more serious thought on the part of the student. On the other hand, it must be admitted that never before were there so many Colleges, Technical Schools, and Institutes for practically all classes of society to choose from, and where every student, no matter what his position, may be certain of obtaining the best instruction. It remains for him to take advantage of his opportunity.

We are afraid it is all too common for the first few months, and sometimes even half the year, to be practically wasted, followed by hurried reading and cramming. This may be all very well for getting through the examination, but it does not leave much good behind it: we therefore earnestly advise all young men now entering on their life-work, to work steadily and continuously throughout the year; they will then retain what they learn and lay a firm foundation for the more serious work which comes after College life.

We by no means advocate sticking too closely to books—"all work and no play makes Jack a dull boy;" a certain amount of exercise and athletics is as essential to keep the body in good health as is our daily food, and it not unfrequently occurs that the old Latin proverb—"Mens sana in corpore sano"—is verified, by the man who is best in the cricket field and in the boat also coming out very near the top in the examinations.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages :—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Sound, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their perparation, and their characteristic tests

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

The first six candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination will respectively receive an Exhibition or a Prize as follows:—The first of such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry two papers will be set and a two days' practical examination.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examiantion, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Christ Church Laboratory.—A. Vernon Harcourt, F.R.S.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar.*

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. Haughton, M.B.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures ofthe Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.* — Elementary, first year; advanced, second year.
2. *Organic Chemistry.* — General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(Division of Engineering, Architecture, and Applied Science).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.

Demonstrator of Practical Chemistry—Herbert Jackson, F.C.S.

Assistant Demonstrator—P. H. Kirkaldy, F.C.S.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1899-1900 are October 3, January 17, and April 25.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Division may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s.; per ann., £8 8s.; Practical Chemistry per term, £4 4s.; per ann., £10 10s.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

Metallurgy.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Photography.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

Evening Classes.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

Faculty of Science.

Professor—William Ramsay, LL.D., F.R.S., &c.

Assistants—Morris Travers, D.Sc., Alexander Kellas, B.Sc., and E. C. C. Baly, F.I.C.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Tuesday, October 3rd, until Friday, December 22nd;

Second Term, from Tuesday, January 16th, 1900, till Friday, March 30th;

Third Term, from Tuesday, April 24th, till Friday, June 29th. Class Examinations begin on June 13th.

Junior Courses of Inorganic Chemistry.

First Term: Tuesday, Thursday, and Saturday at 10., Latter half of Second and Third Term: Tuesday, Thursday, and Saturday. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning on January 9. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday, Thursday, and Saturday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday at 9, and Saturday at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who are studying the subject from a scientific standpoint. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course besides the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1899-1900; also the Clothworker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—W. P. Wynne, D.Sc., F.R.S.

Demonstrators—H. Chapman Jones and M. O. Forster, Ph.D.

Assistants—G. S. Newth, G. T. Morgan, B.Sc., and J. A. Craw.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 5th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics	2	3

Mathematics and Mechanical Drawing, £3 per term. Model and Freehand Drawing, £1 per term. Descriptive Geometry, £3 per session. Mine Surveying, £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half fees.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science and Art Directory may obtain permission to attend free any course of lectures.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses. (See Science and Art Directory).

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-eighth Session will commence on Monday, October 2nd, 1899.

Professors—Chemistry, J. Norman Collie, Ph.D., F.R.S. (Dean); Botany, J. Reynolds Green, Sc D., F.R.S., F.L.S.; Materia Medica and Pharmacy, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the

end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.

Demonstrators—H. Hibbert, B.Sc. (Vic.), and A. Brooke, Ph.D. (Strassburg).

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Tuesday, October 3, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Course; four lectures weekly during the Lent and Easter Terms. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, two lectures weekly on Chemical Theory. (Courses A and B will generally be given in alternate Sessions; for 1899-1900, Course A). (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Wednesdays and Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spentat Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 19, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Alexander Lauder, F.C.S. Assistant Lecturer in Agricultural Chemistry, F. V. Dutton.

Physics. — Professor, Andrew Gray, M.A., LL.D., F.R.S.

The Session opens October 3rd, 1899. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Advanced Inorganic Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 2nd, and terminates on June 22nd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 90 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held,

and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.
Lecturer—Francis E. Francis, B.Sc., Ph.D.
Demonstrator—D. H. Jackson, M.A., B.Sc., Ph.D.

The session 1899-1900 will begin on October 3. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the First and Second Terms. Fee, £3 3s.

General Elementary Science (London Matriculation).—A course of about 16 Lectures will be delivered in the Third Term. Fee, including Physics (1st and 2nd Terms), £5 5.

Special Course.—A special course of Lectures is also given to Engineering Students.

Intermediate Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Junior and Senior Courses.

Advanced Course (Parts I. and II.).—One Lecture a week in each part will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given throughout the Session. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	15	12½	10	7½	5
,, Two Terms ..	11	9	7½	5½	3½
,, One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

General Elementary Science.—A course of Lectures, primarily intended for Candidates for Matriculation, will be given during the First Term. Fee (including Physics), 7s. 6d.

Practical Chemistry — Laboratory Instruction. — The Laboratory will be open two evenings a week from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Secretary.

MASON UNIVERSITY COLLEGE, BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., B.Sc., F.R.S.
Assistant Lecturer—C. F. Baker, Ph.D., B.Sc.
Demonstrator—W. R. Innes, Ph.D., M.Sc.
Lecturer on Metallurgy—Godfrey Melland, F.I.C.

The Session will be opened on October 3rd, 1899.

Elementary Course.

Forty Lectures adapted to the requirements of beginners

will be given in the Winter and Spring Terms. Lecture days—Wednesdays and Fridays at 11.30.

Persons entirely unacquainted with Chemistry are recommended to attend this Course before entering for the General Course. Candidates for the Matriculation Examination of the University of London also are advised to attend this Course.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms) and the Organic Lectures (Summer Term).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Wednesday, and Friday at 9.30. Fee, £1 11s. 6d.

The General Course (including Inorganic and Organic lectures) qualifies for graduation in the medical faculties of the universities of Edinburgh, Glasgow, Aberdeen, and Durham.

Special Courses of Lectures and of Laboratory Instruction are given for Medical Students preparing for the Conjoint Board Examinations.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees :—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; five days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of about £96 is awarded annually in September.

Forster Research Scholarship.—A Scholarship of the value of £50 is annually awarded.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Head Master—W. M. Gardner, F.C.S.

Demonstrator and Lecturer on Geology — Dr. W. F. Sutherst, Ph.D. (Geneva), Chemiste-Diplomé de Zürich.

Lecturer on Botany and Biology—William West, F.L.S.

Assistant—E. Gibson.

The College Session is divided into three terms. The Session commences on September 11th and terminates on July 21st. The course of instruction extends over three years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Fee, £5 per Term, or £13 per Session.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day.

A General Course preparing for the Pharmaceutical Society's examinations has been arranged.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricul-

tural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.
THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc. Lond., F.I.C.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer and Demonstrator—T. S. Patterson, Ph.D.

Demonstrators—J. McCrae, Ph.D., and H. M. Dawson, B.Sc.

The Session begins October, 1899.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Inorganic Chemistry.— Honours Course, Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry.—Honours Course, Non-metals. Tuesday and Thursday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Organic Chemistry Honours Course. — Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry for Teachers.—Saturdays from 9.30 to 12.30 in the first and second terms. Fee, £4 4s.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £5 5s.

Dyeing Department.

Professor—J. J. Hummel, F.I.C.

Lecturer and Research Assistant — A. G. Perkin, F.R.S.E.

Assistant Lecturer—R. B. Brown.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Assistant Lecturer and Demonstrator—Andrew Turnbull, Ph.D.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—J. R. Campbell, B.Sc.

Lecturer in Agricultural Chemistry—H. Ingle, F.I.C.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry — C. A. Kohn, B.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers — T. L. Bailey, Ph.D., C. A. Kohn, B.Sc., Ph.D., and A. W. Titherley, M.Sc., Ph.D.

Assistant—H. H. Froysell.

The Session commences October 2nd.

Entrance Scholarship Examination takes place early in May each year.

The William Gossage Chemical Laboratory has been completed and opened for Advanced Students, the Metallurgical Laboratory has been enlarged, and new Gas Analysis and Electro-Chemical rooms have been added, with a third Lecture Room.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F. — Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metullurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electrochemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Saitanry subjects, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work.

The William Gossage Laboratory, opened in 1897, con-

sists of a large and well-fitted general Laboratory for advanced Students, a new gas analysis room, an additional lecture-room for Metallurgy and other classes, and an addition to the Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Four days	9	16 10s.
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses D and F; Course H. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses D, E, and F. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses D and F, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the Victoria M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for on December 7, 8, and 9, 1899, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Principal not later than November 15. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held on Chemistry, Metallurgy, and on Organic Chemistry.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—Saville Shaw, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturers and Demonstrators—F. C. Garrett, M.Sc., F.C.S., and J. A. Smythe, B.Sc., Ph.D.

The Session will commence on September 25th, 1899.

Lectures begin on October 3rd, 1899.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 5th. Fee, £3 10s. for the Session.

Second Year Course.—The Lectures for the second year students cousist of a course of Lectures on Inorganic Chemistry, extending from October to December, and a course of Lectures on Organic Chemistry from January to the end of the Session. The Class will meet on Tuesdays and Thursdays at 11 a.m., and Fridays at 3 p.m., and will commence on October 6th. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m.

Metallurgy and Assaying.—Lecturer, Saville Shaw, M.Sc., F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the ssubject professed in the College as will enable them to pass the Examinations for the title of Associate in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or stu-

dents who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Science.—Every candidate for the Associateship in Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissibleone year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Wednesday, September 28th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; P. J. Hartog, B.Sc.; E. J. Russell, B.Sc.; D. L. Chapman, B.A.; and H. C. H. Carpenter, B.A.

Demonstrator in Organic Chemistry—W. T. Lawrence, B.A., Ph.D.

Lecturer in Technical Organic Chemistry—Jocelyn F. Thorpe, Ph.D.

Assistant Lecturer in Metallurgy—Dr. Bone.

The Session begins on October 3, 1899, and ends on July 1, 1900.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

Metallurgy.—*Lectures*: The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical*: The Laboratory will be open to students every day.

The Chemical Laboratories are open daily from 9.30. a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the *College* Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; the Levinstein Exhibition; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.

Departments of Chemistry and Metallurgy.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—J. J. Sudborough, D.Sc., Ph.D., F.I.C., and R. M. Caven, B.Sc., F.I.C.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 9th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 5s.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor and Major Examinations. Special lectures will also be given in Chemistry and Materia Medica.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in September. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

An Agricultural Course of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Lecturer—G. Young, Ph.D., F.R.S.E.

The Session will commence on October 6th.

Beginners' Course.—Inorganic Chemistry: Tuesday from 10 to 11 a.m. Fee, £1 11s. 6d.

Matriculation Course.—Friday 10 to 11. Fee, £1 11s. 6d.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 11s. 6d. Honours: Tuesdays and Thursdays, 12 to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 1s. Chemistry of the Colouring Matters: Fridays, 12 to 1; fee, £1 11s. 6d.

Physical Chemistry.—Tuesday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy.—Thursday, 11 to 12. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on the Chemistry of Coal Mining.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—James Walker, Ph.D., D.Sc.

Assistant Lecturers—J. S. Lumsden, Ph.D., B.Sc., and J. K. Wood, M.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 11th, and ends on March 21st. The Summer Session extends from the middle of April to the end of June.

The First Year's Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

A special course of Physical Chemistry will be given during the Summer Session, 1900, including daily Lectures and Practical Laboratory Work.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

The Lectures and Laboratory Practice in Chemistry are recognised by the Medical Colleges of London and Edinburgh. The Courses are suitable for the degrees of the University of London and for the Civil Service appointments, and will also satisfy the requirements of Students in Pharmacy, and of Students who intend to become candidates for the Associateship of the Institute of Chemistry, as far as qualification in Chemistry is concerned.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.
Lecturers—L. Dobbin, Ph.D., and H. Marshall, D.Sc.
Assistants—W. W. Taylor, M.A., B.Sc., J. P. Longstaff, and J. W. Eastham, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are given by the Assistants on some particular branch of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s., Oct.-Dec., Jan.-March; or Summer Session, £5 5s. Half Day—Winter Session, £6 6s., Oct.-Dec., Jan.-March; or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. Practical Examination:—Complex Qualitative Analysis; Inorganic and Organic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on any two of the following subjects, selected by himself:—Ultimate Organic Analysis; Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—F. Grant Ogilvie, M.A., B.Sc., F.R.S.E.
Professor—John Gibson, Ph.D., F.R.S.E.
Assistant Professor—Allan W. C. Menzies, M.A., B.Sc.
Demonstrators—Andrew F. King and Ralph Marshall.

The Session begins October 3rd, 1899.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

Chemistry.—The first course for day students is a combination of Lectures with Laboratory instruction. In the Lectures some of the more important elements and their compounds are discussed in detail, so as to lead to a knowledge of the general laws of chemical action. Other important elements are treated in less detail, and the relations and classification of the elements generally are broadly indicated. In the Laboratory each student will receive instruction in general chemical manipulation, in accurate weighing, volumetric measurements, and in some of the simpler methods of quantitative analysis. After making a series of simple preparations, he works through a number of experimental exercises illustrating chemical combination, oxidation, reduction, and double decomposition. These exercises are followed by instruction in simple methods of qualitative analysis, especial attention being given to dry way testing and the use of the spectroscope. Students attending a further course may take up the study of systematic analysis, and extend the knowledge they have gained of quantitative analysis by exercises in gravimetric, volumetric, and electrolytic methods. Ultimately they may make a speciality of any branch of the subject which may be most necessary for their future work. Great attention has been paid to the thorough equipment of Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—E. J. Mills, D.Sc., F.R.S.
Agricultural Chemistry Lecturer—John W. Paterson, B.Sc., Ph.D.
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1899-1900 may be had from Mr. H. F. Stockdale, the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

United College of St. Leonard and St. Salvator.

Professor of Chemistry — T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 11th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about sixty-four Entrance Bursaries, ranging in value from £40 to £2 15. each per annum, will be held on September 29th and following days. Forty-six of these Bursaries are restricted to Men and about fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. Two of £40 each, and two of £30 each the first year of tenure and £40 the second year, are open to students of either sex. Two Scholarships of £100 each, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1899-1900. A Hall of Residence is provided for Women Students. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a short Course of Laboratory Practice, intended to illustrate the principles of the science.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, and of more advanced Inorganic Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

Scholarships.—In addition to various Scholarships awarded in the Faculties of Arts and Medicine in which Chemistry forms a part of the examination, there are other valuable Scholarships awarded specially in connection with the schools of Chemistry and Physics.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.
Demonstrator—Robert Elliott Doran, F.C.S.

The College Session begins on October 17th, 1899, and ends on June 9th, 1900. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) Two ordinary Courses of Practical Chemistry will be held, each of three months' duration; one commencing on January 5th, 1900, and adapted to the requirements of Students proceeding to the Examinations of the Royal University of Ireland; the other ending about the third week in June, and suitable for Medical Students intending to present themselves for the Examinations of other Licensing Bodies. Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students will be held in the second and third terms; fee, £5. (3) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., F.I.C.

Demonstrator—W. S. Mills, B.A.

The College Session, 1899-1900, commences October 17 and ends June 9.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts. — 1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.* — First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*— First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts. — 1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.* — 1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.* —1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commission for the Exhibition of 1851 offer a Scholarship of £150 per annum. This Scholarship is at present held for a second year by a Chemistry Student of this College.

For Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, STEPHEN'S GREEN, DUBLIN. (SCIENCE AND ART DEPARTMENT).

Professor of Chemistry—W. N. Hartley, F.R.S.

Assistant Chemist—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.

Demonstrator of Chemistry and Assaying — J. Holms Pollok, B.Sc.

The Session commences on Tuesday, October 6th, 1898.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months £12 for the entire session.

The following are supplementary courses of instruction:—

(1) Laboratory Instruction in the Theory of Chemistry. (2) An Analytical Course for Students in Engineering. (3) A Course of Practical Chemistry for Medical Students. (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health. (5) Assaying. (6) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net. — *City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The

courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Tuesday, Sept. 19th, and the Winter Session opens on Tuesday, October 3rd. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 19th, 1899. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting from the Life, and House Decoration.

City of London College, White Street. Moorfields. —Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, A.R.C.S., F.C.S. Session commences September 25.

Battersea Polytechnic.—Principal, Mr. Sidney H. Wells, Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, M.Sc., and Mr. B. C. Polkinghorne, B.Sc. Day and Evening Classes in Science and Art subjects.

Birkbeck Literary and Scientific Institution, Bream's Buildings, Chancery Lane. — Chemistry Courses will be conducted, commencing September 26, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University, by Mr. J. E. Mackenzie, Ph.D., B.Sc.

Borough Polytechnic Institute, 103, Borough Road (near the Obelisk).—Chemistry: Evening Lectures and Laboratory Work (Session fees, per course, 3s. to 15s.), Dr. F. Mollwo Perkin, assisted by Dr. A. J. Walker. Physics: Evening Lectures and Laboratory Work (Session fees, per course, 6s. to 10s.), Dr. J. Henderson. Session opens Monday, September 25, 1899.

Brixton School of Chemistry and Pharmacy, 12, Knowle Road, Brixton.—Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c. The Lectures and Classes are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to Degrees at the University of London. Medals and certificates are awarded to successful students, The Laboratory is fitted with every convenience for the prosecution of chemical studies and research. Prospectuses and further information may be obtained from the Principal.

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University Tutorial College, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Corr. Coll.).—The next Session commences on Monday, October 2nd. Work may be taken up in the Laboratories for short periods, or in systematic classes extending for one or more terms. Special facilities are offered to country students for work during the ordinary vacations. During last year, students of University Tutorial College carried off over £1000 in Hospital and Entrance Scholarships, and at the recent Science Examinations (July, 1899) of London University, no less than 155 students were successful.

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NOTE ON BUTTER ANALYSIS.

By W. LAWRENCE GADD, F.I.C.

ONE of the most valuable and widely used methods of examining butter is the determination of the amount of alkali required to neutralise the volatile fatty acids, originally due to Reichert. As the figures afforded by this method of analysis commonly determine, to a large extent, whether adulteration is indicated or not, it is of the first importance that the process should be as free as possible from any source of error; and, furthermore, should, under similar conditions, give the same results in the hands of different analysts.

A recent experience in connection with a sample of butter suspected of adulteration, showed that exactly concordant results are not always obtained by two or more chemists working on the same sample when the estimations are carried out in the usual manner. This led me to undertake some experiments, which are not yet complete, but the first results of which justify the publication of this note.

In Reichert's test, as ordinarily carried out, the saponification of the butter fat is effected by heating with approximately semi-normal alcoholic potash, prepared from methylated spirit which has been re-distilled with caustic potash. This solution, as is well known, is liable to change with age, even when kept in closely stoppered bottles, and it occurred to me that this might be a source of error in making the Reichert test.

To ascertain this, a solution of caustic potash in alcohol (A) was carefully prepared in the usual way, and stored in a well-stoppered bottle. Another similar solution (B) was also prepared and kept in a flask, which was loosely closed by an ordinary cork, for three weeks before using. This solution rapidly darkened in colour (by oxidation) and became much the darker of the two solutions. The Solution A was employed at intervals of a few days to estimate the volatile fatty acids in a sample of butter fat carefully prepared from genuine butter, and gave numbers ranging from 14 c.c. to 12·2 c.c. Solution B, after keeping for three weeks, gave, with the same sample of butter fat, 19·3 c.c. to 20·6 c.c. for 2·5 grms. of fat.

Side by side with each of these determinations, an estimation was made on the same butter fat in the following manner:—

About 2·5 grms. of the butter fat (which should be only just melted, and on the point of solidification) is accurately weighed in an 8-oz. flask; 20 c.c. of methylated spirit, freshly distilled with caustic potash, and about 1 grm. of solid potassium hydrate, are added, and the flask plunged into hot water. The potash rapidly dissolves in the alcohol, and the butter fat is saponified in a very short time. The flask is heated in the water-bath until all trace of alcohol is evaporated off, filtered air being blown in from time to time, and the soap spread evenly over the inner surface by turning the flask round and round to facilitate the evaporation.

When all smell of alcohol is gone, 50 c.c. of distilled water are added, and the soap dissolved by gently heating the flask on the water-bath. After cooling the solution, 20 c.c. of a 10 per cent solution of pure sulphuric acid are then added, together with a few pieces of broken porcelain, the flask attached to a condenser, and exactly 50 c.c. distilled off. The distillate is filtered, the receiver and filter washed two or three times with warm water, and the filtrate titrated with N/10 sodium hydrate, using a single drop of phenolphthalein as indicator.

By this method it was found that practically the same results were given by a sample of butter fat after forty days' keeping as when freshly prepared, although in the interval the fat had changed slightly and had become bleached perfectly white. The following are the actual results obtained:—

	Alcoholic potash.			Solid caustic.		
Age.	Fat taken.	N/10 NaOH required.	N/10 NaOH for 2·5 grms. fat.	Fat taken.	N/10 NaOH required.	N/10 NaOH for 2·5 grms. fat.
Days.		C.c.	C.c.		C.c.	C.c.
			Solution A.			
1	2·564	13·0	12·6	2·560	16·0	15·6
7	2·517	14·1	14·0	2·516	16·4	16·2
11	2·551	13·8	13·5	2·559	16·5	16·1
13	2·552	12·8	12·5	2·529	16·3	16·1
16	2·527	12·4	12·2	2·527	16·5	16·3
			Solution B.			
23	2·515	19·3	19·1	2·577	16·3	15·8
39	2·552	21·1	20·6	2·501	16·0	15·9
45	2·533	21·0	20·7	2·555	16·4	16·0

From these figures, it will be seen that the change undergone by alcoholic potash on keeping has a serious effect upon the accuracy of Reichert's test, and, in extreme cases, probably renders the estimation valueless. On the other hand, by using fresh alcohol and solid potash in the manner described, concordant results are obtained even with fat several weeks' old.

THE ANALYSIS OF BINARY ALLOYS.

ABOUT two years ago an attempt was made to analyse some brasses, without separating the copper and zinc, by taking advantage of the respective behaviour of the two metals with standard potassium cyanide in an alkaline solution. By completely discharging the blue colour of the ammoniacal copper solution, and then adding potassium iodide, and going back with silver nitrate to a faint silver iodide turbidity (CHEMICAL NEWS, lxxvi., p. 189), the copper, when alone, was accurately estimated, but the zinc, unfortunately, under the above conditions, was so very irregular in its indications that the alloys in question had to be analysed by other means.

The principle of the process seems to have some merit, and as I am unaware of its having been previously suggested I venture to give it here, in the hope that some one may have an occasion to make use of it, my own opportunities of doing so, at present, not being apparent.

Let A and B be the two constituents of the alloy, and X and Y the amount of standard solution they respectively utilise. Let M c.c. be the amount of solution the weighed amount of alloy actually needed, and M' the calculated amount it would need if it all happened to be A; also let the ratio—determined, if necessary, by experiment—between equal weights of A and B be R.

Then,—

$$X + Y = M \text{ and } X = M - Y,$$

but—

$$Y = \frac{M' - X}{R};$$

so—

$$X = M - \frac{M' - X}{R} = \frac{MR - M'}{R - 1}$$

The same conclusion is reached by regarding—

$$X = M - \frac{M' - M^*}{R}$$

as an approximate expression, and then continually substituting for the asterisked M the value—

$$M - \frac{M' - M^*}{R},$$

and summing the series.

This very clumsy way is the one in which I first worked out the expression—

$$X = M - \frac{M' - M}{R - 1},$$

which is identical with—

$$\frac{MR - M'}{R - 1}.$$

If R = 1 the process is valueless. It becomes increasingly accurate as R differs from 1; supposing, of course, the titrations remain equally reliable.

J. T.

ON THE PURIFICATION OF ACETYLENE BY MEANS OF ACID SALINE SOLUTIONS.

By ALBERT R. FRANK.

In a recently published paper (*Zeit. f. Angew. Chem.*, Nos. 40-41, 1898), Dr. Wolff passes in review the methods of purifying acetylene which give the best results. In the first place we find that of Lunge and Cederkreutz, improved by this author (Dr. Wolff), a process which depends essentially on the oxidation by chloride of lime of the impurities which accompany acetylene. He also describes the process I proposed, which consists of using acid saline solutions to absorb the impurities; then the ammonia is neutralised by the acid, while the sulphuretted hydrogen is precipitated in the state of metallic sulphide, and the phosphoretted hydrogen is absorbed.

Wolff gives the preference to his process, since, according to him, the use of acid saline solutions has great drawbacks, but it is not at all necessary to use saline solutions in the liquid state; it is, on the contrary, preferable to impregnate porous bodies, especially kieselguhr, with these solutions; in this manner the volume occupied by the purifying material is very much diminished, and the method is particularly adapted to small plants. The above-mentioned author seems to think that by using my method the choice of apparatus would present certain difficulties, and he is of opinion that the use of metallic vessels should *à priori* be condemned. He is, however, in error; in most branches of chemical industry apparatus of enamelled iron has for a long time been used, and has given every satisfaction; they resist the action of the most concentrated acids, even when warm. It is also incorrect to imagine that acid saline solutions can cause explosions; this might apply to solutions of copper, on account of the formation of acetylide of copper, but my solutions are prepared in such a manner that the copper is precipitated in the state of sulphide long before the whole of the acid becomes neutralised by the ammonia, even if the latter be present in the gas in very large proportions.

The purifying material consists of a very acid solution of cuprous chloride, or of an acid solution of ferric chloride of known strength; and these solutions do not attack, neither do they decompose, the acetylene gas in any way. One kilogrm. of ferric solution is enough to purify 7 to 10 cubic metres of acetylene, and the same quantity of the cuprous solution is enough to purify 18 to 25 cubic metres of this gas without being exhausted. Further, in the case of cuprous solutions, the exhausted purifying material can be easily regenerated.

It suffices to boil the cuprous solution after having freed it from the precipitate of cuprous sulphide; in this manner we can eliminate the phosphoretted hydrogen, which is never found in the state of phosphide, but simply in a state of rather unstable combination, easily decomposable by heat. The solution is now ready to use again after a certain amount of copper has been added, and it has been brought up to its original volume by means of hydrochloric acid.

When we have to deal with, as has generally been the case up till now, an acetylene apparatus supplying 20 or 30 lamps, each burning five or six hours a day, and each consuming 20 litres of gas an hour, it suffices to have a purifying apparatus capable of holding 12 to 15 kilogrms. of purifying material. This quantity is enough to last three or four months, and when it commences to become exhausted we notice a diminution of the lighting power, and the formation of phosphoric acid, and sulphuric and anhydride fumes. Even when the material no longer absorbs phosphoretted hydrogen and sulphuretted hydrogen, there still remains a quantity of acid more than sufficient to absorb the whole of the ammonia, and the formation of easily decomposable metallic acetylides is impossible.—*Zeitschrift für Angewandte Chemie*, 1898, p. 1050.

ON THE COMPOSITION OF THE FATTY OIL EXTRACT OF CEDAR NUTS.

By M. D. KRYLOFF.

Cedar-nut oil may become an important article of commerce in view of the abundance of the cedar forests in the northern districts of Russia in Europe, and Siberia. Unfortunately the exploitation of these forests is still in a very primitive state. At the exhibition at Nijni-Novgorod in 1896, the firm of Fedtcherxo and Gridassof exhibited some cedar oil, a sample of which has been used by the author for his experiments.

The sample examined was a thick transparent liquid, with a golden straw-yellow colour. Its density at 0° was 0·9326. At −20° the oil did not solidify, but simply became thicker.

The following table gives the constants of cedar oil compared with those of some other oils:—

	Index of iodine.	Reichert-Meissl index.	Saponification index.	Acid index.
Linseed oil ..	158—178	0·95	190—192	0·4—1·1
Cedar oil ..	149·5—150·5	2·0	191·8	1·09
Hemp-seed oil	143—144	—	192—194	0·64—4·82
Sunflower oil	19·9	0·5	193—194	—
Olive oil ..	81·6—84·5	1·5	191—193	1·66

We see that cedar oil does not differ much from other oils as regards its composition.

The fatty acids extracted from the oil gave a crystalline deposit which has been separated. The semi-solid mass was spread out on porous plates, and then re-crystallised several times in alcohol. This substance melts at 63°, and on analysis gives figures corresponding to the formula $C_{16}H_{32}O$. It was thus shown to be palmitic acid.

The liquid fatty acids which are found in the filtrate were oxidised with permanganate of potash, and the separated oxy-acids were purified by boiling in alcoholic solution with animal charcoal, and then fractionally crystallised; three fractions were thus obtained. Fraction I., the most considerable, melting at 165°; fraction II., melting at 159°—161°; and fraction III., the smallest, melting at 140°.

The first fraction consisted of tetroxy-stearic acid, and the last fraction of dioxy-stearic acid containing a small quantity of tetroxy-stearic acid.

The conclusion to be drawn from these experiments is that cedar oil resembles linseed oil with regard to its composition, and may be looked upon as belonging to the class of siccative oils.—*Journal Rouss Physico-Chim. Obchtchestra*, 1898, p 9248.

THE AFTER-FORMATION OF GAS IN ACETYLENE GENERATORS.

By P. WOLFF.

An inherent fault in all acetylene generators is the after-formation of gas, which takes place after the direct contact between the carbide and the water has ceased. This generation is due to the action of the residual water contained in the pores of the carbide, to the condensation of water on the surface of this carbide, and also to the absorption of aqueous vapour.

The author has measured the quantity of gas thus liberated by 1 kilogrm. of carbide by passing it through a meter. In one series of experiments the carbide reservoir was over water; in other experiments it was over petroleum. The results showed that in the latter case the quantity of gas formed amounted to 0·25 litre at the end of the first half hour, to 6 litres after twenty-four hours, and then remained constant at 16 litres at the end of three days. In the first case, on the other hand, 7·5 litres were collected in half an hour, 25 litres in twenty-four hours, and 30 litres at the end of three days; after that, the liberation of gas continued at the rate of from 5 to 6 litres per day, until the integral decomposition of the carbide was complete.

These figures show in a very plain manner the considerable risks of explosion which are incurred by the use of small generators, and table lamps in particular. This danger can be avoided in large apparatus by using a reservoir of sufficient capacity to hold the excess of gas without undue compression.

Different means have been proposed for obviating this inconvenience, especially the use of a layer of petroleum to separate the carbide from the water; but this method is not practicable—for, on the one hand, a very thin layer of petroleum does not prevent the evaporation of the water; and, on the other hand, with a thick layer there would be a risk of close contact with the carbide, which would be then rendered impervious to water.

The most efficacious method appears to be that of Münsterberg. A valve closes all communication between the carbide reservoir and the water as soon as the former has been raised; the after-formation of gas is therefore no longer produced, except by the water contained in the pores of the carbide. Further, in Münsterberg's apparatus the gas reservoir is of large size, so that the proportion of air introduced at the same time as a fresh charge of carbide is no more than 20 per cent; that is to say, below the limit of explosive mixtures.—*Metallarbeiter*, xxiv. (16), p. 122.

ON THE PRESENCE OF AMMONIA IN RAW ACETYLENE.

By Dr. HEINRICH BAMBERGER.

From the point of view of their origin, the deleterious foreign bodies which accompany acetylene may be divided into two classes; the bodies which are derived from the raw materials used in the preparation of the carbide (phosphoretted hydrogen, sulphuretted hydrogen), and secondly, the bodies formed during the operation of electric fusion (ammonia and compounds of cyanogen). The presence of those first mentioned may be avoided, to a certain extent, by the use of raw materials of as great purity as possible, but as far as concerns ammonia it is necessary to take the very greatest precautions in the operation of fusion itself.

The injurious action of the ammonia contained in the acetylene is much greater than that exercised by phosphoretted hydrogen and sulphuretted hydrogen, for these two bodies are transformed during the combustion of the acetylene into nitro-oxygenated compounds. What we therefore have to do is to eliminate this body, which is fortunately not at all a difficult operation.

During the decomposition of the carbide of calcium by water, the ammonia is formed at the expense of two different compounds, the nitrides and the cyanogenated compounds. The formation of nitrides is due to the presence of either aluminium or of magnesium in the lime.

Nitride of magnesium, Mg_3N_2, is formed simultaneously with the oxide during the combustion of the magnesium; water decomposes it, even in the cold, into oxide and ammonia. It is true that up to the present we have not succeeded in finding magnesium in the carbide, but the magnesia contained in the lime is reduced by the electric current to the metallic state, and thus gives rise to the nitride.

It must be remembered that a certain quantity of air is always circulating through the electric furnace, and that the carbons, the crucibles, and the braizes always contain a certain quantity of nitrogen; this explains the formation of the nitride.

On the other hand, aluminium is found in greater or less quantities in almost every variety of lime, as well as in carbon, under the form of more or less impure alumina. In the presence of carbon, alumina is reduced to the metallic state, and the metal combines by combustion in air with the nitrogen. Like the corresponding compound of magnesium, nitride of aluminium also causes, under the same conditions, the formation of ammonia. The second source of this body is furnished by the compounds of cyanogen.

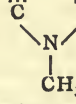
The carbides have the property of absorbing nitrogen at a high temperature, and of forming cyanogenated compounds. The formation of ammonia at the expense of these compounds is due to a saponification which takes place under the influence of superheated steam.

A large number of analyses have shown that acetylene contains from 0·05 to 0·15 per cent (by volume) of ammonia.—*Zeitschrift für Angewandte Chemie*, 1898, p. 720.

ON THE ACTION OF FUMING NITRIC ACID ON SOME CYCLIC COMPOUNDS OBTAINED BY SYNTHESIS.

By Dr. H. KUNZ-KRAUSE.

It has recently been shown that Vitali's reaction may serve to show the presence of the methylimide group,—



in the heterocyclic annular compounds, and also to what point it will serve for this purpose, and consequently for the recognition of the constitution of natural alkaloids.

Starting from this point, the author thought it would be of interest to extend his research to the so-called aromatic compounds, in which the atom of nitrogen does not form part of the ring, but serves as a lateral link of an isocyclic annular system. The anilines and anilides are compounds of this nature. The anilides, and first among them acetanilide, and the analogous compounds occupy, thanks to their recent employment in medicine, a place of great interest in pharmacy. It seemed advisable to apply the research to this group of bodies first of all.

The carrying out of the experiments referred to later on was effected in the manner described in the previous research on the subject of the reaction of carbylamine. As with these former, the following reactions have been obtained in every case, with 0·2 grm. of material, and 3 c.c. of fuming nitric acid at 1·5 density, and by repeating

the experiment at least three times. In certain cases, and, above all, when the results were negative, these were checked by control experiments repeated several times. For performing these experiments, the same porcelain crucibles as used in the previous experiments were found to give the best results. The mixture was evaporated down on a boiling water-bath, and the residue was left until the reaction described further on took place. The observations made on each compound are taken into consideration in the following résumé.

When I commenced the series of experiments with acetanilide, I made the surprising observation that the product of the action of the acid, which existed in the form of a reddish-brown residue, was distinguished by a property which could hardly have been predicted by theory; this was its spontaneous inflammability. On this account it seemed advisable to first examine the anilides in this connection, and to endeavour to answer the following questions:—

1st. Should we find in this behaviour of acetanilide a characteristic reaction of value for its identification? or, 2nd, is it common to the other derivatives of acetanilide and to other anilides? Can we, in this case, find any relationship between the reaction and the constitution of the bodies in question?

Experiment has decided in the latter sense, as will be shown by a study of the results.

I would strongly advise that the experiments be carried out in a closed space, and that, as a precaution against violent inflammability, not more than 0·2 grm. of products liable to form spontaneously inflammable compounds should ever be used.

I. *Acetanilide.*—This body dissolves easily without any violent action, taking a greenish-brown colour. The reaction does not become stronger, except after the addition of relatively large quantities of fuming nitric acid. The latter part of the experiment is of greater interest. The original greenish-brown solution becomes a reddish-yellow, then a deep red, then brown, and, finally, when it is almost completely evaporated down, a very deep blackish brown. At this moment the residue suddenly takes fire, and a tall column of brilliant flame, charged with soot, shoots up from the crucible. The residue, after the extinction of the flame, has an odour of nitrophenol, which changes to that of aniline on the addition of an aqueous solution of soda-lye.

As this reaction is certain, even when we only use 0·14 grm. of acetanilide, and as, on the other hand, it does not take place with the analogous compounds recently used in medicine, with the exception of *p*-bromide of acetanilide, or *o*-tolylacetamide, it merits a certain amount of attention, from the practical point of view, as a sure and simple method of detecting this substance. Repeated trials with different quantities have proved that the reaction reaches its lower limit with 0·14 grm. of material, while with 0·15 grm. we always obtain a large flame; ignition no longer takes place with 0·13 grm. By using 0·14 grm. we always obtain a spontaneously inflammable residue, if the evaporation has been carried out in a porcelain crucible as has already been recommended.

II. *Acet-o-toluide* (*o-Methylacetanilide*).—After a lively reaction, we immediately obtain an orange-yellow solution. The residue from the evaporation, which is spongy and of an orange-red colour, ignites spontaneously and burns, leaving a light spongy mass of carbon.

III. *p-Chloride of Acetanilide.*—Vapours of hyponitric acid are given off in large quantities from the orange-yellow solution, and suddenly a brilliant flame, charged with soot, shoots up from the crucible; the residue, unlike that from acetanilide, does not appear to be carbonised, but remains orange-yellow in colour, and continues to give off luminous vapours at short intervals, giving rise to fresh explosions, a characteristic test for the *p*-halogen-acetanilides (see the following compound).

The residue is a dry yellowish-brown mass. By using 0·14 grm. of the material and 3 c.c. of fuming nitric acid I was enabled to observe nearly twenty spontaneous ignitions, the last one being particularly bright.

IV. *p-Bromide of Acetanilide.*—This body behaves in the same manner as *p*-chloride of acetanilide. With 0·20 grm. of material, three consecutive spontaneous ignitions were obtained. I would here mention a method, elaborated on the occasion of the present research, for the better preparation of this compound. It is certainly preferable to the ordinary method, which consists of introducing the calculated quantity of bromine into the acetic solution of acetanilide: we dissolve in a porcelain dish 12 grms. of acetanilide in 2 litres of water, heating gently. After cooling, an equally cold solution of 14 grms. of bromine in distilled water is added to the filtered solution until it becomes yellow. The precipitate of *p*-bromide of acetanilide is washed with cold water, and dissolved in boiling water to obtain pure crystals. The normal fusing point of the product thus obtained is 166°.

V. *p-Nitroacetanilide.*—This behaves in an analogous manner to that of the two *p*-halogen-acetanilides. By using 0·20 grm. of material, I noted an ignition of the brown residue from the evaporation, which was repeated three times.

VI. *Benzoanilide.*—The residue from the evaporation of the greenish-brown, and afterwards brownish-yellow solution, is of a soft consistency, and of an orange-red colour. It does not ignite spontaneously.

VII. *Acetylacetanilide.*—In spite of the great speed of the reaction, the yellowish-brown residue does not ignite spontaneously; this distinguishes it from the acetanilide. The introduction of a second acetyl group, in the arrangement of the atoms of the first, annihilates the inflammability of the nitrogen compounds of acetanilide.

VIII. *Methylacetanilide* (*Exalgine*).—The solution, which is bright yellow, is easily obtained. After heating, there results, after a lively reaction, an olive-green solution. The syrupy brownish-yellow residue is not spontaneously inflammable.

IX. *Acet-p-toluide* (*p-Methylacetanilide*).—The reaction is very violent, and is accompanied by a large disengagement of nitrous vapours. We immediately obtain an orange-red solution. The residue from the evaporation does not ignite spontaneously, but burns very fiercely on the approach of a flame.

X. *Acetyl-o-amidophenol.*—The reaction is impetuous, and produces a greenish-brown solution, which keeps on disengaging large quantities of vapour. The final residue does not ignite either spontaneously or on the approach of a flame.

XI. *Acetyl-p-amidophenol.*—This reaction, which is also very brisk, furnishes an orange-red solution, giving off large quantities of nitrous vapours, and the residue of which, after evaporation, is a greyish-yellow. It will not ignite either on the approach of a flame or spontaneously.

XII. *p-Methoxyacetanilide* (*Methacetine*).—The residue from the evaporation of the solution does not ignite spontaneously, in spite of the violence of the reaction, accompanied by a considerable disengagement of nitrous fumes. It will only ignite, but then easily, on actual contact with a flame. Its colour is brownish-yellow.

XIII. *p-Ethoxyacetanilide* (*Phenacetine*).—The action is extraordinarily violent. The product of the reaction, which is first a yellowish-red, then brownish-red, does not ignite spontaneously, and does not give off carbylamine either with an aqueous or alcoholic solution of potash. Treatment with an aqueous solution of potash lye produces an odour of fresh pears.

XIV. *Aceto-p-sulphanilate of Sodium* (*Casaprine*).—The reddish-brown residue does not ignite spontaneously, but contact with a flame causes it to burn brilliantly, accompanied by a deposit of soot.

XV. *Acet-p-amidosatol* (*Salophene*).—The brownish-black residue does not ignite spontaneously, but burns quietly, without forming soot, on contact with a flame.

XVI. *Oxalanilide.*— In spite of the violent reaction

which takes place on the addition of acid, it was not possible to obtain a spontaneous ignition of the pulverulent, white residue, even when using 0·5 grm. of material.

XVII. *α-Acetonaphthylamide.*—The solution obtained, after a very vigorous reaction, is of an orange-red colour; the residue from its evaporation does not ignite spontaneously, but only on contact with a flame, when it detonates and produces a large quantity of carbon and soot.

XVIII. *β-Acetonaphthylamide.*—This reaction, which is still more violent than the preceding one, produces a greenish-black solution, which gives off continuously hyponitric fumes. The residue only ignites on contact with a flame, and its combustion proceeds very quietly.

XIX. *Ethoxy-ana-benzoylamidochinolene* (*Analgene*).—The reddish-yellow solution gives, on evaporation, an orange-red residue, with a very strong odour of benzoin. It does not ignite either spontaneously or on contact with a flame.

From the above it appears that of all the bodies examined up to the present there are, besides acetanilide itself, only the parachloride and parabromide of acetanilide, nitroacetanilide, and orthomethylacetanilide, which produce, by evaporation with fuming nitric acid, residues which ignite spontaneously.

We are able to deduce the following conclusions which are of great interest from the theoretical point of view:—

1st. Spontaneous ignition, which characterises the product of the reaction of fuming nitric acid on acetanilide under the conditions described above, takes place when strongly electronegative elements or molecules—Cl, Br, NO_2—are found in the para-position of the acetamide group. The same holds good for the group CH_3 in the ortho-position.

2nd. Spontaneous ignition does not take place—

(*a*) When the electro-positive groups—CH_3, OCH_3, OC_2H_5, or OH—or the molecules of SO_2ONa, or of the more complicated acids, $C_6H_4{<}^{OH}_{CO}$, are found in the para-position to the acetamide group.

(*b*) When the group OH takes the ortho-position to the acetamide group. This cannot, consequently, replace the CH_3 group.

(*c*) When the atom H, still unplaced in the acetamide group, is replaced by CH_3.

(*d*) When the acetyl molecule is replaced by another acid one; or, finally,

(*e*) When the benzoylic nucleus is replaced by the naphthalene or chinolene nucleus—*Pharm. Zeit.*, Berlin, 1898, No. 94.

ANALYTICAL METHODS FOR DISTINGUISHING BETWEEN NITROGEN OF PROTEIDS AND NITROGEN OF SIMPLER AMIDES OR AMIDO-ACIDS.

By J. W. MALLET,
Professor of Chemistry, University of Virginia.

Discussion of Materials and Conditions.

It is admitted by all who have had experience in the chemical analysis of materials used as food that the common practice of determining the total nitrogen in such materials, by multiplying the result by 6·25 and calling the product so obtained "protein," is but a crude and clumsy way of approximately representing the value of the material under examination as respects its nitrogenous constituents. Besides the substances which are properly designated as proteids, there are other nitrogenous constituents of food materials which differ widely from these in nutritive value, and some of which also differ greatly from these and from each other in the proportion of nitrogen which they contain.

Classes of Nitrogenous Constituents in Foods.

The following classes of the nitrogenous constituents of food are commonly recognised as requiring separate consideration:—

1. Proteids proper (by some called albumenoids), and their closely related derivatives, the proteoses and peptones.

2. Gelatinoids or collagens, and allied substances immediately derived from them, such as gelatin, chondrin, &c.

3. Simpler amides, amido-acids, and allied substances, such as the asparagin, glutamin, &c., of vegetable materials, and the "flesh bases" (creatin, creatinin, &c.), of animal origin.

4. Alkaloids, or amine-like compounds of well-determined basic character.

5. Ammonia and its salts.

6. Nitrates.

To these, no doubt, should be added lecithin and analogous substances containing nitrogen, but closely allied to the fats.

The known and commonly used methods for determining nitrogen in the forms of ammonia and nitrates, which occur but sparingly in food materials, may be considered fairly satisfactory. Alkaloids in the commonly accepted sense of the term demand attention only in connection with such special accessories of food as tea, coffee, and similar nervous stimulants, and the chief substances of alkaloidal character admit of being separately dealt with in these special cases without serious trouble and with a fair degree of accuracy.

It is with the first three of the above-named classes of food constituents that difficulty is encountered, and for which further study of methods is desirable. The object of the work which the writer has undertaken, and to which he has devoted a good deal of time for several months past, has been to study the means of distinguishing between the first and third of these classes of constituents, the proteids and related bodies on the one hand, and the simpler amides and amido-acids—sometimes grouped together as "nitrogenous extractives"—on the other. Incidentally only, some experiments have been made with representatives of the gelatinoid class.

Nutritive Values of Three Classes.

It is commonly assumed that proteids, gelatinoids, and the simpler amides have very different nutritive values, and, while all authorities would agree in assigning the highest value to the first of these, there is probably no small difference of opinion as to the order in which the second and third should be rated. In considering such a question, there should be separately taken into account relative digestibility or solubility, capability of undergoing osmotic absorption, and oxidisability in order to the production of energy. At present no definite numerical statement of the relative nutritive values of nitrogenous bodies of these three classes can be made. It seems much to be desired that more extended experiments than have so far been recorded should be made upon living animals—as far as possible upon human beings—in regard to the utilisation of both the gelatinoids and the simpler amides. The latter no doubt undergo oxidation to some extent in the animal body, and produce some energy in consequence. It is probably true of these simpler amidic substances that much larger quantities than analysis exhibits as constituents of the food consumed, or than analysis detects among the residua of food rejected from the body without having undergone complete oxidation, may be constantly formed among the earlier products of the metabolism of the proteids, and afterwards themselves undergo further change into the simpler and more stable forms of carbon dioxide, water, and urea.

Lack of Precision in Chemical Constitution.

It must be admitted that to a chemist the question of distinguishing between the proteids and the simpler

amides is not one of a scientifically precise character. The proteids doubtless contain at least a part of the nitrogen in the amidic relation, and where the line is to be drawn between more complex and more simple amides is, of course, more or less a matter to be arbitrarily decided. But of greater importance still is the doubt whether any of the so called proteids are entitled to recognition as definite chemical substances. We usually understand by the term "a definite chemical substance" a substance of which all the molecules are exactly alike in constitution. Thus to the chemist the identity of such a substance as pure common salt, or cane sugar, or caffeine, depends on the absolute identity in character of all the myriad molecules of which even the smallest sensible mass is made up. But in regard to such materials as these we are able to determine the relative and absolute number of atoms of the elements of which each molecule is composed, and in many cases their order of attachment to each other, or the "structure" of the molecule. On the other hand, we have reason to believe that the so-called proteids are made up of molecules of such extreme complexity, assemblages of such large numbers—hundreds—of atoms of carbon, hydrogen, oxygen, and nitrogen, that we can make but random guesses at their arrangement, and cannot even determine with any certainty their number, relative or absolute. We talk of albumen, myosin, syntonin, as if these terms stood for pure chemical substances in the same sense that attaches to ammonia, benzene, or urea. But it is by no means certain that in a specimen of the most carefully prepared albumen from blood or white of egg any hundred, or any ten, molecules are absolutely alike. It may well be that a minute specimen of such a material consists in reality of numerous more or less similar, but yet in some respects different, molecules, which we lump together under a single name merely because they have a general resemblance, with certain properties in common. Furthermore, in nutrition investigations we have to deal with articles of food representing complex mixtures of substances referable to the two classes of the proteids and nitrogenous extractives, with many other things besides. Hence, an answer to the question to be examined must be a limited one, and such only as may serve the limited purpose of practical application in connection with nutrition investigations. Any process of separation, to be of value in such application, must be reasonably simple, and capable of being carried out without too great consumption of time.

List of Substances Examined.

A good deal of work was necessary at the outset in procuring satisfactory specimens of the several substances to be examined. Some of these have been prepared out and out in this laboratory from natural animal or vegetable sources. Some have been purchased in a more or less crude state and carefully purified. Some have been purchased and their purity ascertained by testing.

The following representatives of the simpler amidic and imidic compounds were experimented with:—

Amido-acids of the fatty series:—
Glycocin (glycocoll or amido-acetic acid).
Alanin (*a*-amido-propionic acid).
Leucin (amido-caproic acid).

Amido-acids of the succinic acid and allied series:—
Aspartic acid (amido-succinic acid).
Asparagin.
Glutamic acid (*a*-amido-oxyglutaric acid).
Glutamin.

Amido-acid, including a benzene nucleus:—
Tyrosin (oxy-phenyl-*a*-amido-propionic acid).

Betaine bases:—
Betaine.

Guanidine bases:—
Kreatin.
Kreatinin.

Bases and neutral amides related to uric acids:—
Hypoxanthine (sarkine).
Carnine.
Allantoine.

As representatives of the proteids and allied substances the following were used:—

Albumen, from white of egg.
Albumen, from blood.
Fibrin, from blood.
Casein, from milk.
Legumin, from peas.
Globulin (para-globulin), from serum of blood.
Vitellin, from yolk of egg.
Myosin, from muscular tissue.
Syntonin (acid albumen), from muscular tissue).
Hæmoglobin (mainly oxyhæmoglobin), from blood corpuscles.
Albumose, from egg albumen.
Peptone, from fibrin of blood.
Gelatin, from skin.
Chondrin, from cartilage.

Solutions used in Experiments.

These were, for the experiments by precipitation, brought into solution as follows, involving, as will be seen, change of chemical constitution in some cases:—

Albumen, Hæmoglobin, } dissolved in cold water.

Gelatin, Chondrin, } dissolved in hot water.

Fibrin, brought sparingly into solution by prolonged action of a 10 per cent solution of sodium chloride in water.

Fibrin, digested with a 4 per cent solution of caustic soda, and the solution afterwards acidified with acetic acid.

Casein, dissolved in 1 per cent solution of caustic soda, and the solution cautiously treated with dilute acetic acid to an extent just short of coagulation.

Globulin, dissolved in 5 per cent solution of sodium chloride.

Vitellin, Myosin, } dissolved in 10 per cent solution of sodium chloride.

Syntonin, dissolved in 0·1 per cent solution of hydrochloric acid.

Albumose, from the early stage of digestion of egg albumen by means of pepsin and 0·2 per cent solution of hydrochloric acid.

Peptone from advanced stage of digestion of blood fibrin hy means of trypsin and 0·25 per cent solution of sodium carbonate.

Foods Involved in the Investigation.

While it was especially desirable to ascertain the behaviour of these several substances, of both classes, in their separate condition, it was borne in mind that in connection with nutrition investigations they have to be dealt with as constituents of ordinary food materials, principally the following:—

Meats, including poultry and fish (raw and cooked), soups and stews, meat extracts, eggs, milk and cheese, bread and other farinaceous preparations such as cakes and pastry, fruits and raw table vegetables, cooked fruits and table vegetables, fruit conserves, undigested and unabsorbed residues of food.

It was assumed as probable that the same method in detail) would not be best adapted to all cases, but would be likely to need modification in application under different conditions.

Of course, the investigation undertaken has gone over ground already well trodden, and the results recorded by Schulze, Barbieri, Sachsse, Kormann, Boemer, Huefner. Allen, Tankard, Chittenden, Osborne, Wiley, and others, have been carefully examined.

The experimental work of the present investigation is reported, not altogether in the order in which it was done, but rather in logical succession, taking account first of physical differences, between the classes of substances to be distinguished, then of the effects of chemical agents of decomposition, and, lastly, of relations to solution and precipitation.

(To be continued).

CONTRIBUTION TO THE KNOWLEDGE OF THE RUTHENOCYANIDES.

By JAS. LEWIS HOWE.

POTASSIUM ruthenocyanide was described by Claus, in 1854, in his "Beiträge zur Chemie der Platinmetalle." The salt was formed by fusing ammonium rutheninitrosochloride (Joly, *Comptes Rendus*, 1889, cviii., 854; Howe, *J. Am. Chem. Soc.*, 1894, xvi., 388), tetrachloride of Claus, with potassium cyanide. The attempt was also made to form it by fusing potassium ferrocyanide with ruthenium, but it was found impossible to separate the ferrocyanide and ruthenocyanide, It is probable that some of Claus's experiments were carried out with a ruthenocyanide contaminated with ferrocyanide, from the fact that he describes copper ruthenocyanide as brown, whereas, when free from the ferrocyanide, it is pale green. Potassium ruthenocyanide in reactions and crystallisation resembles very closely the ferrocyanide, except that when pure it is white. Its crystallography as well as that of the isomorphous ferrocyanide and osmocyanide are described by A. Dufet (*Comptes Rendus*, 1895, cxx., 377).

Preparation of potassium ruthenocyanide for the purpose of carrying out experiments upon it not yet completed, gave occasion to the work recorded in this paper.

In the Claus method of preparation, a large proportion of the ammonium rutheninitrosochloride is decomposed with separation of metallic ruthenium, and while a part of the ruthenocyanide formed crystallises out from a solution of the melt, in large square pseudorhombic plates, much is left in the solution, and cannot be directly separated from the potassium cyanide and other salts present. Attempts were therefore made to use other methods of formation, with the following results:—

1. Potassium rutheninitrosochloride, K_2RuCl_5NO, fused with potassium cyanide, gave rather better results in ruthenocyanide, there being rather less decomposition than was the case with the ammonium salt.

2. Ruthenium trichloride, $RuCl_3$, fused with potassium cyanide, gave a fair product of ruthenocyanide.

3. Metallic ruthenium, fused with potassium cyanide, was slightly acted upon, giving a trace of ruthenocyanide.

4. Metallic ruthenium, fused with potassium cyanide and a little potassium hydroxide, gave rather stronger reaction than case 3, but the amount of ruthenocyanide formed was very small.

5. The melt formed by fusion of ruthenium in potassium hydroxide and nitrate, containing potassium ruthenate, K_2RuO_4, was dissolved in water, and boiled with potassium cyanide. The deep orange-red solution was quickly decolourised, and the ruthenium was converted into ruthenocyanide with little loss. A considerable proportion could be obtained in the usual square crystals. This process could, by modification, probably be made the most satisfactory method of forming the ruthenocyanide, presenting one decided advantage that metallic ruthenium, or oxides, can be used, thus avoiding the necessity of preparing the nitrosochloride or chloride.

6. Ruthenium trichloride was boiled with a strong solution of potassium cyanide. The ruthenocyanide, crystallising in the usual square form, was obtained, but very much contaminated with a greenish by-product not yet investigated, probably analogous to Prussian blue.

7. Potassium rutheninitrosochloride was boiled with a strong solution of potassium cyanide. The solution was slowly decolourised, considerable of the greenish by-product being formed. From this solution there crystallised thick straw-coloured hexagonal plates, which will be considered further on. The quantity of the product is not satisfactory.

8. The Weselsky method (Weselsky, *Sitzber. Akad. Wien.*, 1870, lx., [2], 261; *Ber. d. Chem. Ges.*, 1869, ii., 588) of forming double cyanides was tried. Hydrocyanic acid was led into a solution of the nitrosochloride, in which barium carbonate was suspended until effervescence ceased. The solution gave no reaction for ruthenocyanide. Its colour had changed to the brown-yellow of the trichloride, but gave no reaction for this with potassium thiocyanate, or with ammonia and sodium thiosulphate. On warming, the solution gelatinised to a firm hydrogel, insoluble in hot aqua regia, but soluble in boiling potassium hydroxide. This last solution was unchanged on acidification with hydrochloric acid, and gave the potassium ferrocyanide reaction for nitrosochloride, but no reaction for trichloride. The dried jelly was easily explosive on heating. It presents an interesting analogy to Jackson's (*Ber. d. Chem. Ges.*, 1896, xxix., 1020) hydrogel of cobaltocyanide, and is being further studied.

9. The Weselsky method was also applied to ruthenium trichloride. The merest trace of ruthenocyanide was formed, and the solution, little changed in colour, no longer gave reactions for the trichloride.

10. The nitrosohydroxide of Joly, formed by the precipitation of the chloride by potassium carbonate, is easily soluble in potassium cyanide, and converted into ruthenocyanide by prolonged boiling.

The following reactions of ruthenocyanide may be noted:—

No precipitates are formed with the caustic alkaline earths, their ruthenocyanides being soluble in water.

Lead acetate gives a fine white precipitate, soluble in nitric acid.

Silver nitrate gives a white curdy precipitate, insoluble in both ammonia and in nitric acid.

Ferric chloride gives a rich purple precipitate, closely resembling Prussian blue in its chemical properties. In pure water it is soluble, but is precipitated from this solution by salts or alcohol. It forms a very beautiful and intense dye, adhering with great persistence to cotton fibre on which it has been precipitated. It is decomposed very readily by alkalis with precipitation of ferric hydroxide, re-forming, however, on the addition of acids, unaffected by dilute acids, but permanently decomposed by strong acids. It is a most delicate reaction for the detection of ruthenocyanide.

Ferrous sulphate gives a pale blue precipitate, which gradually changes to the purple above mentioned, and instantly if bromine water is added.

Copper sulphate gives a very pale green flocculent precipitate (not brown as given by Claus).

With salts of the following metals precipitates are formed insoluble in hydrochloric acid:—Cadmium, white (soluble in hot acid); zinc, white; tin (both stannous and stannic), white; mercury, white; bismuth, white (insoluble in nitric acid); nickel, dirty green (changing to blue with hydrochloric acid); cobalt, pale red; platinum, yellow-green; manganese gives a white precipitate soluble in hydrochloric acid. With gold there is no immediate precipitate, but a gradual darkening and separation of a dark precipitate, the solution becoming green.

Bromine water changes the solution to a dark red, which does not give the trivalent ruthenium reaction. Iodine also seems to alter the solution.

No reaction with hydrogen sulphide, ammonium sulphide, or thioacetic acid.

Nitric acid has no effect in the cold, but when heated slightly reddens the solutions. It then shows no signs of a reaction analogous to that of the nitroprussides.

	Theory for $Ba_2Ru(CN)_6,6H_2O$.	From $RuCl_3$ and KCN solution.	Found. From $RuCl_3NO$ by fusion.			From $RuCl_3NO$ by solution.		
		I.	II.	III.	IV.	V.	VI.	VII.
Barium	42·90	—	—	—	42·46	43·32	42·27	42·54
Ruthenium	15·86	16·41 (with SiO_2)	15·67	—	15·72	17·92 (with SiO_2)	15·80	15·60
$5\frac{1}{2}H_2O$ (100°)	15·67	15·67	15·63	—	15·68	—	—	15·53
$6H_2O$ (200°)	16·83	16·68	16 85	—	16·69	16·71	16·56	16·68
5C	9·37	—	—	—	—	—	—	—
6C	11·23	—	—	—	—	—	—	—
C from combustion.. ..	—	—	—	9·91	9·16	9·96	—	9·98
C in residue	—	—	—	2·65	2·03	—	—	2·30
Total carbon	—	—	—	12·56	11·19	—	—	12·28

It is acted on by potassium nitrite with sulphuric acid, and when neutralised gives a fugitive rose-red with ammonium sulphide.

It gives no apparent reaction with ruthenium trichloride or nitrosochloride.

Two methods of purification, applicable to such portions of the ruthenocyanides as cannot be separated by crystallisation, may be used. The most satisfactory is the precipitation in dilute solution by lead acetate and thorough washing with hot water to remove any lead chloride present. Suspension of the lead ruthenocyanide (carbonate, cyanide, &c.) in much water and decomposition with dilute sulphuric acid. Filtration and addition of baryta water till nearly neutral, and then of barium carbonate in excess; warming, filtration, and evaporation to crystallisation of the barium ruthenocyanide from which other ruthenocyanides may be formed by double decomposition.

The other method of purification which is applicable especially to all residues, is precipitation with ferric chloride in slightly acid solution, washing with acidified water, as far as possible (the purple begins to dissolve as the salts are washed out), and decomposing with baryta-water. This method, while very useful for recovery of residue, does not give so pure a product as the first method.

The hexagonal crystals described above, in Process 7, presented points of interest, in that it seemed not impossible that they contained the nitroso-group of the nitrosochloride from which they were formed. When dissolved in water they showed every reaction of the ordinary square crystals of the ruthenocyanide, but they could not be converted into the square form by re-crystallisation, nor could their yellowish tint be removed. The crystals are anhydrous, while the white crystals contain three molecules of water of crystallisation. On heating they explode with considerable violence, while the square crystals decompose very gently. On re-crystallisation they show prismatic forms, with many twins resembling staurolite crosses, and others resembling aragonite twins. Though perfectly hexagonal in form, they do not seem to belong to the hexagonal system. After conversion into the lead, hydrogen, barium, and back into the potassium salt by the first method of purification described, and further precipitation of this potassium salt by alcohol and re-crystallisation from water, crystals were obtained which were square, white, and in every respect—crystallographically as well as chemically—resembled the ordinary potassium ruthenocyanide. This was verified by analysis of the barium salt and partial analysis of the potassium salt.

It is evident that the hexagonal crystals are not a nitrosocyanide, and it seems possible that the form may be conditioned by some trace of impurity. They are being further studied at present.

Analysis of Potassium and Barium Ruthenocyanides.

Potassium Ruthenocyanide, $K_4Ru(CN)_6,3H_2O$, formed by boiling a solution of potassium rutheninitrosochloride with potassium cyanide; purified by conversion through lead, hydrogen, and barium salts.

	Per cent.
I. Loss of water in four days standing over sulphuric acid	10·84
II. Loss of water at 120°	10·90
III. Loss of water in thirty hours standing over sulphuric acid	11·25

Theory for $K_4Ru(CN)_6,3H_2O$ .. $3H_2O$ = 11·53

The crystals, especially when small, are so efflorescent that it is difficult to obtain uneffloresced salt for analysis, and the following are calculated for the dehydrated salt.

	Theory for $K_4Ru(CN)_6$.	Found. I.	II.	III.
Potassium.. ..	37·76	37·22	38·32	37·28
Ruthenium ..	24·53	23·90	24·22	24·44

This corresponds to the potassium ruthenocyanide described by Claus.

Barium Ruthenocyanide, $Ba_2Ru(CN)_6,6H_2O$ (new), formed from the ordinary form of the potassium salt.

Pale straw-coloured diamond-shaped (up to ½ c.m. long) monoclinic crystals, or larger crystal rosettes, slightly soluble in cold, more easily in hot water, slowly lose water of crystallisation over sulphuric acid, lose $5\frac{1}{2}$ molecules of water at 100°, but retain ½ molecule to nearly 200°, thus resembling barium ferrocyanide. The barium ruthenocyanide from the hexagonal form of the potassium salt was similar, but was not obtained in well enough defined crystals to identify positively with the preceding, but analysis shows the constitution to be the same.

The method of analysis was the following:—The salt was heated in a platinum boat (in two cases porcelain was used and attacked, so that the ruthenium was contaminated by silica—Analyses I. and V.) in an oxygen current, and the carbon dioxide evolved collected in an absorption apparatus. The proportion given off was variable, but usually a little more than 5 atoms. The boat was then heated in a hydrogen current, to reduce the oxide of ruthenium formed. The boat was then placed in a carbon dioxide apparatus and treated with hydrochloric acid, and the remainder of the carbon dioxide collected. The barium chloride was then filtered off from the ruthenium and determined as sulphate; the ruthenium, after burning the filter-paper and heating in a hydrogen current in a porcelain boat, was estimated as the metal. It was not found possible to arrive at any agreement in different analyses as to the loss on heating the barium salt in air, or oxygen, or subsequently in hydrogen. While most of the carbon of the cyanogen is burned to carbon dioxide, a part remains as barium carbonate. The remainder of the barium seems to fluctuate between oxide and peroxide, while a variable portion of the ruthenium is oxidised. The analyses show conclusively that six atoms of carbon are present in the salt derived from the nitrosochloride, hence one cyanogen group cannot be replaced by the nitroso-group.

The results of several analyses are given in the accompanying table.—*Journal of the American Chemical Society*, xviii., No. 11.

DETERMINATION OF CARBON IN IRON AND STEEL WITHOUT COMBUSTION APPARATUS.

By GEORGE T. DOUGHERTY, Chicago.

THERE has been a need of long standing for a reasonably quick and simple method of determining both kinds of carbon in iron and steel, with accuracy of results equalling the standard method of combustion in oxygen, or with sulphuric and chromic acids. Methods for estimating graphitic carbon, one among them by Eggertz, the father of the carbon colour test, are given in text-books; but all of them prescribe details or conditions which result in ruining their success for quick filtering or accurate work, and have been almost universally abandoned as giving too crude estimations. It is desirable to avoid gelatinising the silicon as much as possible, for silica freshly separated retains more or less hydrated water when dried at 100—115° C. Nitric acid diluted dissolves titanium carbide and other carbides, while dilute hydrochloric acid will not do quite as much, and usually leaves a dirty looking residue, which requires washing with caustic potassa, alcohol, and ether. The following method for graphite I have designed to overcome all difficulties or objections, and, judging by my own experience as proved by checks with irons containing known quantities of graphite, leaves very little to be desired for simplicity of operations and reliability of results.

Method for Graphite.

Dissolve 1 grm. of pig or cast iron drillings in 60 c.c. of nitric acid, 1·135 sp. gr. (the same acid as is used for rapid phosphorus work); heat gently until all are dissolved, and boil a few minutes to cook the combined carbon entirely into solution. Do not evaporate unduly, or use stronger acid, or much less acid of the specified strength, for more silicon would gelatinise and increase the insoluble residue. Have weighed previously a Gooch crucible, with its lid and cap, and put a disk of ashless filter-paper (about the area of a dime or penny) in the crucible and weigh again. Fit the Gooch crucible with the paper disk in it in the filtering bottle in connection with the filter pump in action, and pour water in to cause the paper to adhere perfectly to the bottom of the crucible. Now filter the solution of the iron, and wash five times with hot 10 per cent nitric acid, and once or twice with hot water. This operation of filtering and washing usually need not consume more than ten or fifteen minutes with good suction. Dry the crucible and contents to constant weight at 115—120° C. on the hot plate under a large inverted broken beaker with an opening in the top for a thermometer, which should touch the hot plate. This apparently crude air bath desiccates 100 to 200 per cent more quickly than the regulation copper air bath, probably because it allows of a constant current of air. The increase of weight (*a*) over the tare of the crucible and paper disk represents graphite and other insoluble residue. Burn off the graphite over a good Bunsen burner and weigh again when cool. The increase of weight over the tare of the crucible alone gives the amount (*b*) of siliceous residue. The difference between *a* and *b* indicates the quantity of graphite. The residue, which is silicon with sometimes a little iron oxide, usually amounts to from 0·0005 to 0·0040 grm., and the amount of hydrated water retained in the dried insoluble residue cannot on this small quantity of silica have amounted to anything to be allowed for in ascribing the entire loss on ignition to graphite. The graphite thus obtained burns off much more expeditiously than when it has been deposited on tared or counterpoised filters as used in the several old methods. Counterpoised or tared filters frequently give "shaky" results as in the determination of other elements. Paper disks (ashless), owing to their very small areas, are constant in weight, and are certain to filter more quickly than asbestos layers in Gooch crucibles at all times. Besides, the asbestos filter is found to retard the burning of graphite, since you cannot by means of a platinum wire very well press the latter against the red-hot walls of the crucibles.

Two Methods for Combined Carbon.

1. The well-known colour method, which need not be described in detail here, may generally be applied with considerable safety if you know the previous history of irons to be tested, and have a standard iron of similar treatment whose carbon is not too widely different. White or mottled iron, for instance, cannot be reliably read off with a soft iron standard. Steel standards may be used, if they have been found by actual experiments to correspond well with various irons of known carbon contents. I have on hand such a steel standard (0·31 per cent carbon), which is, of course, more convenient to use than a standard pig or cast iron, since steel drillings are uniform in carbon, and do not require filtering when dissolved, while the whole lot of iron drillings must be mixed well on paper every time they are required, or segregation of graphite will ultimately occur with disastrous consequences. I do not, however, attempt to use that steel standard with irons of high combined carbon; in a case of recent occurrence it would show 2·64 per cent of combined carbon in a sample of white iron which had actually 2·49 per cent. The colour method is, therefore, of limited value unless performed under certain conditions, and these conditions must be religiously adhered to. When the carbon in a sample of iron or steel is so low that its solution appears greenish instead of brownish when read in the camera behind the usual ground glass in daylight, or when artificial light is required, a thin slab of porcelain (such as they make lamp shades of) in the place of ground glass before an electric light will be found to remove entirely the green shade of low carbon tests, and bring out different tints of brown colour quite sharply and unmistakably.

2. The alternate method, which is more universal in application, and, like the one given above for graphite, aspires to equal the "old reliable" combustion process, is similar in some of the operations to the graphite method, and is as follows:—

Pour on 1 or 2 grms. of drillings in a dry beaker 60 or 100 c.c. of a slightly warm 33 per cent solution of double chlorides of copper and potassium, acidulated with 5 per cent of strong hydrochloric acid. Frequent or continual stirring greatly promotes the solution of the copper thus displaced. As for graphite, weigh the Gooch crucible alone, and again with a paper disk in it. Turn on suction, pour water on, and then the copper and iron solution, wash twice with hot dilute hydrochloric acid (1 acid to 3 water), twice with hot water, four times with hot nitric acid of 1·135 sp. gr. (this to dissolve out copper sulphide and any particle of metallic copper), and finally twice with hot water. Dry to constant weight at not exceeding 120° C. on the hot plate, taking more care regarding temperature than is necessary for graphite. The increase of weight over that of the crucible and paper disk represents the quantity (*a*) of graphite, organic compound, and insoluble siliceous residue, with often a little copper oxide. Burn off the graphite and organic compound and weigh again. The amount (*b*) of residue after ignition is shown by the increase of weight over the tare of the crucible alone. Deduct *b* from *a*, and the remainder (*c*) is graphite plus organic compound. Again deduct from *c* the amount of graphite elsewhere determined; the remainder (*d*) is organic compound, which multiplied by 0·675 gives the amount of combined carbon. This method seems to be fully equal to the elaborate standard combustion process, and has the advantage of being simpler and quicker, with fewer possible sources of error. Some time ago I happened to find out that combined carbon set free by the double chloride of copper and potassium did not deposit in the form of pure carbon as commonly supposed, but of an organic compound of unknown composition, and I pro-

ceeded to standardise its actual percentage of carbon, which was done by treating by the method just described three steel standards of different carbons, which I had on hand, namely, 0·17, 0·31, and 0·48 per cent. The average of the results obtained, which, by the way, were pretty close, gave 67·50 per cent of carbon, which I have adopted as the factor on the organic compound, which is certainly deserving of further study. If an asbestos filter be used instead of a paper disk it would require a factor rather lower, but does not give equally satisfactory or uniform results.

It may prove interesting by way of illustration and comparison to subjoin the results of a recent analysis of standardised cast iron drillings marked A, and furnished by the Standardising Bureau of the American Foundrymen's Association, whose official figures for that sample are 3·11 per cent graphite and 0·56 per cent combined carbon, the average of combustion determination by four different parties:—

1 grm. taken for graphite.

	Grms.		Grms.
	14·0263		14·0682
Crucible = ...	14·0255	Crucible + disk = ..	14·0362
Residue after ignition = ...	0·0008	Total matter on drying = ...	0·0320
		Residue after ignition = ...	0·0008
		Loss by ignition =	0·0312

0·0312 × $\frac{100}{1}$ = 3·12% graphite.

1 grm. taken for combined carbon.

	Grms.		Grms.
	14·0268		14·0820
Crucible = ...	14·0252	Crucible + disk = ..	14·0415
Residue after ignition = ...	0·0016	Total matter on drying = ...	0·0405
		Residue after ignition = ...	0·0016
		Loss by ignition =	0·0389
		Graphite = ...	0·0312
		Organic compound =	0·0077

0·0077 × 0·675 × $\frac{100}{1}$ = 0·52 % combined carbon.

By colour with 0·31 % carbon steel standard .. .. .. { 0·51 % combined carbon. 0·52 % combined carbon.

Before concluding this article it will be important to point out that the last method given above is not applicable to ferromanganese without considerable modification in the details of the operation and in the factor used for calculation. Copper is an elementary constituent of the organic compound containing the carbon of ferromanganese separated by potassio copper chloride; and it would be unsafe to use a platinum Gooch crucible with a paper disk for estimating it, since copper would be reduced from its combination and attack the bottom of the crucible, as it has done in my experience. In such a case, unless one has an arrangement for passing oxygen gas into the crucible during the ignition, an asbestos layer may be used in lieu of a paper disk. Instead of 0·675 as for iron and steel, the factor would be 0·80 or more, depending largely on the mode of operation. I purpose to investigate and work out more fully this point later.—*The Iron Age.*

Reducing Properties of Boron and of Aluminium.—MM. Duboin and Gauthier.—If boron and silicon are mixed intimately with alumina in a porcelain tube, the whole then raised to a very high temperature and a current of chlorine passed along the tube for some time, chloride of aluminium and boric acid are formed.—*Comptes Rendus*, cxxix., No. 4.

NOTICES OF BOOKS.

Die Aetherischen Oele. Von E. GILDEMEISTER und FR. HOFFMANN. Bearbeitet im Auftrage der Firma Schimmel und Co., in Leipzig. Berlin: Verlag von Julius Springer. 1899. Pp. iv., [ii.], 919. Roy. 8vo. Ill.

THIS monumental work forms a practical and scientific encyclopædia on essential oils in all their bearings, botanically, chemically, and commercially; it is divided into three main parts—a historical introduction of 95 pages; a general treatise on the theoretical extraction, the occurrence, and valuation of essential oils (in 185 pages); and a special part which gives the history, origin, extraction, properties, composition, valuation, and statistics of each of 422 oils.

In the preparation of this comprehensive work, the firm of Schimmel and Co. secured the services of several competent authors: Dr. Friedrich Hoffmann, many years resident in New York City, but now of Berlin, wrote the historical introduction, the history of the raw materials furnishing the oils, and the account of the American products; for the balance of the work Dr. Edward Gildemeister is responsible, with the exception of two chapters by Dr. C. von Rechenberg and by Dr. J. Helle.

The handsomely printed volume shows thoughtful care throughout; the typography and heavy paper leave nothing to be desired; the illustrations are excellent, notably the full-page pictures of modern distilling apparatus at pages 129—136. Two admirable maps—one showing the avenues of commerce in the Middle Ages, and one of Sicily showing the region of cultivation of oranges and lemons—are good features. Another excellent feature are the very numerous references to literature as footnotes, that constitute a veritable bibliography.

The historical introduction by Dr. Hoffmann shows deep research; it is agreeably illustrated by facsimiles from early woodcuts of quaint appearance.

The special part contains a mass of information not easily found elsewhere, and makes an invaluable work of reference for those interested in the subject.

A good index closes the handsome volume.

H. C. B.

The Analysis of Minerals. (Traité d'Analyse des substances minerales). By A. CARNOT. Membre de l'Institut, Inspector-general of Mines, &c. Vol. I. Paris: Vve. Ch. Dunod. 1898. Pp. 992.

THIS magnificent work, of which the first volume is now before us, has been written with the idea of making known the present state and the applications of mineral chemistry. The author has devoted himself to this subject for over thirty years, and during this time has examined all kinds of minerals, rocks, metals, mineral waters, &c. In the present volume he has arranged and co-ordinated the large number of documents which have accumulated during this long period, in the hope that his experience will be of profit to young chemists.

About one half of the volume is devoted to qualitative researches, and the remainder to general operations of quantitative analysis, the details of which will fill two more volumes to follow.

The early chapters deal with examination by the dry way, blowpipe analysis, spectroscopic methods, microchemical examination, &c., followed by the methods of the wet way. The author has devised a new system by means of which not only the commoner elements can be detected in very complex mixtures, but also the numerous so-called rare earths which modern progress in chemistry no longer allows us to pass over. This important subject commences on page 201, and continues to page 296. This is followed by a chapter on the principal characteristics of the bases and acids corresponding to the different elements, and a chapter on the preparation and use of reagents, and their purification.

The second part commences with instructions as to taking samples of materials often very heterogeneous in character; numerous details are given on means of heating, forms of apparatus to be used, and precautions to be taken for preventing causes of error in the weighing of bodies, &c.

Special chapters are devoted to electrolytic methods, volumetric analysis by saturation, oxidation, reduction, precipitation, and colorimetry.

The last chapter deals with the qualitative and quantitative analysis of gas, and of gaseous mixtures.

We have no doubt that this volume will be highly appreciated by all chemists, old and young, and we congratulate the author on its production.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 5, July 31, 1899.

Isomeric Forms of Chromic Acetate.—A. Recoura.—In a recent paper the author describes two of the isomeric forms of chromic acetate. The present communication contains an account of the preparation and properties of the remaining two forms—(1) A second violet acetate, or chromo-mono-acetic acid, with formula $Cr(C_2H_3O_2)_3H_2O$, a substance which in the solid state and in solution is a violet colour. It is not a true chromium salt, but a monobasic acid. It is produced by the spontaneous transformation of the dibasic acid, which takes about ten days. The reaction can be expressed by the equation—

$$Cr(OH)_2(C_2H_3O_2)(C_2H_4O_2)_2 = H_2O + Cr(OH)(C_2H_3O_2)_2.C_2H_4O_2.$$

(2) Green chromo-mono-acetic acid, with formula $Cr(C_2H_3O_2)_3.\frac{1}{2}H_2O$, is green both in the solid state and in solution. It possesses properties very similar to those of the violet acid. It is produced by the spontaneous transformation of the solution of the violet acid. The action is very slow, probably taking a year, but is rendered very rapid by boiling the solution of the violet acid with acetic acid. The reaction may be expressed by the equation—

$$2 \text{ molecules } Cr(OH)(C_2H_3O_2)_2(C_2H_4O_2) = H_2O + 1 \text{ molecule } Cr_2O.(C_2H_3O_2)_4(C_2H_4O_2)_2.$$

Action of Magnesium on Saline Solutions.—Georges Lemoine.—Magnesium decomposes water very slowly at ordinary temperatures, but in the presence of certain salts, and with the magnesium in the form of powder, the action becomes very lively. Taking, for example, the chloride, the following action probably takes place:— $MgCl_2 + mMg + mH_2O = MgCl_2 + mH_2 + mMgO$. The author has measured the gas evolved after varying times, and has studied this reaction thermochemically.

Dissociation of Hexammoniacal Cadmium Chloride.—W. R. Lang and A. Rigaut.—The authors have investigated the dissociation of combinations of ammonia with anhydrous cadmium chloride, using liquefied ammonia-gas and powdered cadmium chloride. They determined the tensions of dissociation of hexammoniacal cadmium chloride, and found that above 62° the compound $CdCl_2 6NH_3$ cannot exist.

Dissociation of Mercury Diammonium Iodide.—Maurice François.—Ammoniacal mercuric iodide does not behave in the same manner as ammoniacal silver chloride; its dissociation shows the existence of a white intermediate compound. During the first period of dissociation, $HgI_2.2NH_3$ decomposes into ammonia gas and into the compound $3HgI_2.4NH_3$ without the production of mercuric iodide. This decomposition is characterised by a strong dissociation tension. During the second period, the compound $3HgI_2.4NH_3$ is decomposed into mercuric iodide and ammonia; the dissociation tension being very slight.

Action of Sodammonium and Potassammonium on Selenium.—C. Hugot.—The selenides of sodium and potassium, obtained by the action of sodammonium and potassammonium on selenium, present properties almost identical. The two salts correspond to the formulæ Na_2Se_4 and K_2Se_4. This method of their preparation gives the compounds in a very high state of purity.

Some Acetylacetonates.—G. Urbain and A. Debierne.—The authors describe the preparation and properties of acetylacetonates of iron, manganese, cobalt, chromium, aluminium, and nickel. A comparison of the properties of these compounds shows the analogy between the sesquioxides of cobalt and manganese, and those of aluminium, iron, and chromium. Not only in all the acetylacetonates of the sesquioxides is the metal trivalent, but the physical and chemical properties are nearly identical. Their crystalline forms are also analogous; they melt without decomposition, and are all more or less volatile. They all combine with two molecules of chloroform when crystallised from this solvent.

No. 6, August 7, 1899.

Thermo-chemical Determinations. Ethylenediamine.—M. Berthelot.—The present paper contains some determinations, following on those already published, for the investigation of the principles which underlie the production of animal heat and chemico-biological syntheses. These were carried out on the acids of bile, amygdaline (a very widely distributed glucoside in vegetable fruits, and which produces hydrocyanic acid and the essence of bitter almonds), conicine (the acid of hemlock), and, finally, ethylenediamine (the most simple type of bivalent alkaloids containing more than one nitrogen atom, which play so important a part among the therapeutic alkalis).

Ammoniacal Nitrate of Silver.—MM. Berthelot and Delépine.—The employment of ammoniacal nitrate of silver in certain calorimetric measurements, led the authors to make a complete study of this compound, which represents in reality the nitrate of a complex stable ammoniated base, forming two stable salts in solution. The base is as powerful as the mineral alkalis.

Action of Chlorine on a Mixture of Silicon, Silica, and Alumina.—Emile Vigouroux.—A mixture of silica and aluminium can be used to prepare chloride of silicon. This preparation takes place in two stages—(1) The reduction at a red heat of the silica by aluminium and the exhaustion by acids of the powder obtained. (2) The attack of the residue, when completely freed from acid, by chlorine.

Action of Phosphoretted Hydrogen on the Oxide, Hydrate, and Carbonate of Copper.—E. Rubenovitch.—Hydrogen phosphide attacks copper oxide immediately, at first slowly, then more energetically, a considerable quantity of heat being evolved. In the case of the hydrate, the action is so violent that the substance is rendered incandescent. To moderate the reaction, the gas must be admitted into the presence of the hydrate in small quantities at a time. The carbonate used in this experiment is the one obtained by precipitating copper sulphate with carbonate of soda, $CO_3.Cu.Cu(OH)_2.5H_2O$. The action of hydrogen phosphide on this substance is represented by the equation—

$$5PH_3 + 5CO_3.Cu.Cu(OH)_2 = 2P_2Cu_5 + H_3PO_4 + 5CO_2 + 11H_2O.$$

The phosphide obtained is greyish black, amorphous, and very soluble in nitric acid and bromine water.

Some Properties of Dioxyacetone in Relation to the Degree of Molecular Aggregation. — Gabriel Bertrand.—Dioxyacetone can exist in two forms, each having distinct properties and a different molecular state of aggregation. The study of these forms, and the conditions under which they pass from one to the other, permits of an explanation of certain physical anomalies of dioxyacetone, such as superfusion and supersaturation.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following information was received too late for insertion in the "Students' Number":—

NORTHERN POLYTECHNIC INSTITUTE, Holloway Road, N.—Head of Chemical Department: The Principal, J. T. Dunn, D.Sc.; Assistant Lecturers, Mr. H. Charles L. Bloxam, and Mr. W. H. Watson, A.R.C.S.; Secretary, Mr. E. Griffiths. Session begins September 25th. Evening Classes in Practical and Theoretical Inorganic and Organic Chemistry, 6 to 9.30 p.m., open to Students of either sex. The courses at present arranged extend over a period of four years. Instruction is also given in Elementary Chemistry applied to the Arts and Manufactures. A special course of demonstrations will be given on the theory and principles of Chemical Analysis. There is a special laboratory for Gas Analysis, and every facility is given for the prosecution of research. The Physical Department is under the charge of Mr. Victor A. Mundella, B.A., B.Sc. Besides the usual courses in Physics, an introductory course on Elementary Experimental Science (Mechanics, Physics, and Chemistry) is given conjointly by the Principal and Mr. Mundella.

STOCKPORT TECHNICAL SCHOOL. — Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application. Special instruction is given in the Dyeing of Felt, &c., as applied to Hat Manufacture.

QUEEN'S COLLEGE, BELFAST.—The Session commences on Tuesday, October 17th, 1899.

Institute of Chemistry of Great Britain and Ireland. July-August Examinations, 1899. — *Names of Candidates who passed the Intermediate Examination*:—A. W. Comber, Finsbury Technical College, London; J. Cooper, B.Sc. (Durham), Durham College of Science, Newcastle-on-Tyne; L. Eynon, Finsbury Technical College, London; W. Eyre, University College, Sheffield; J. Fotheringham, Glasgow and West of Scotland Technical College; W. A. Fyffe, University College, Dundee; H. Hall, University College, Nottingham; W. H. Jollyman, Finsbury Technical College, London; A. G. Levy, Finsbury Technical College, London; J. A. Lloyd, Mason University College, Birmingham; S. E. Melling, Owens College, Manchester, and under A. H. Allen, Esq., F.I.C.; W. G. Orme, Mason University College, Birmingham; C. J. Silverston, B.Sc. (Lond.), Mason University College, Birmingham; W. H. Taylor, Finsbury Technical College, London; V. W. Theobalds, Finsbury Technical College, London; H. L. Wall, Finsbury Technical College and University College, London. *Names of Candidates who passed the Practical Examination for the Associateship.*—P. Auchinachie (for Fellowship), under Cecil H. Cribb, Esq., F.I.C.; W. B. Clark, Glasgow and West of Scotland Technical College, and under J. Hornby, Esq. F.I.C.; C. R. Darling, Royal College of Science, Dublin; R. N. S. Doresa, Merchant Venturers' Technical College, Bristol, and under Dr. E. H. Cook, F.I.C; E. Goulding, B.Sc. (Lond.), Registered Student under Professor W. R. Dunstan, M.A., F.R.S., F.I.C.; J. Kerr, B.Sc. (Edin.), Registered Student under Dr. Stevenson Macadam, F.I.C. *Names of Candidates who passed the Final Examination for the Associateship.*—In Branch "A" (Mineral Chemistry: W. S. Denham, Glasgow and West of Scotland Technical College; E. R. Nind, A.C.G.I., City and Guilds of London Central Institution; J. G. A. Rhodin (for Fellowship), University of Upsala, Sweden, and under J. Wilson Swan, Esq., F.R.S., F.I.C.; J. H. Smith, Assoc. R.C.Sc. (Lond.), Royal College of Science, London. In Branch "B" (Metallurgical Chemistry): J. P. de Castro, B.A. (Cantab.), Cambridge University, and under Sir William Roberts-Austen, K.C.B., F.R.S.; W. T. Collis, Mason University College, Birmingham. In Branch "D" (Organic Chemistry): R. D. Abell, University College of North Wales, Bangor; W. A. Cates, Finsbury Technical College, London; R. L. Jenks, A.C.G.I., City and Guilds of London Central Institution.

NORTHERN POLYTECHNIC INSTITUTE,
HOLLOWAY ROAD, N.

Principal and Head of Chemical Department—J. T. DUNN, D.Sc.
Assistants—H. CHAS. L. BLOXAM, W. H. WATSON, A.R.C.S.

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RICHARD MARTIN, Secretary.

THE CHEMICAL NEWS.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

DOVER, 1899.

INAUGURAL ADDRESS OF THE PRESIDENT,

PROF. SIR MICHAEL FOSTER, K.C.B., SEC.R.S.

HE who until a few minutes ago was your President said somewhere at the meeting at Bristol, and said with truth, that among the qualifications needed for the high honour of Presidency of the British Association for the Advancement of Science, that of being old was becoming more and more dominant. He who is now attempting to speak to you feels that he is rapidly earning that distinction. But the Association itself is older than its President; it has seen pass away the men who, wise in their generation, met at York on September 27, 1831, to found it; it has seen other great men who in bygone years served it as Presidents, or otherwise helped it on, sink one after another into the grave. Each year, indeed, when it plants its flag as a signal of its yearly meeting, that flag floats half-mast high in token of the great losses which the passing year has brought. This year is no exception; the losses, indeed, are perhaps unwontedly heavy. I will not attempt to call over the sad roll-call: but I must say a word about one who was above most others a faithful and zealous friend of the Association. Sir Douglas Galton joined the Association in 1860. From 1871 to 1895, as one of the General Secretaries, he bore, and bore to the great good of the Association, a large share of the burden of the Association's work. How great that share was is perhaps especially known to the many men, among whom I am proud to count myself, who during his long term of office served in succession with him as brother General Secretary. In 1895, at Ipswich, he left the post of General Secretary, but only to become President. So long and so constantly did he labour for the good of the Association that he seemed to be an integral part of it, and meeting as we do to-day, and as we henceforward must do, without Douglas Galton, we feel something greatly missing. This year, perhaps even more than in other years, we could have wished him to be among us; for to-day the Association may look with joy, not unmixed with pride, on the realisation of a project in forwarding which it has had a conspicuous share, on the commencement of an undertaking which is not only a great thing in itself, but which, we trust, is the beginning of still greater things to come. And the share which the Association has had in this was largely Sir Douglas Galton's doing. In his Address as President of Section A, at the meeting of the Association at Cardiff in 1891, Professor Oliver Lodge expounded with pregnant words how urgently, not pure science only, but industry and the constructive arts—for the interests of these are ever at bottom the same—needed the aid of some national establishment for the prosecution of prolonged and costly physical researches, which private enterprise could carry out in a lame fashion only, if at all. Lodge's words found an echo in many men's minds; but the response was for a long while in men's minds only. In 1895 Sir Douglas Galton, having previously made a personal study of an institution analogous to the one desired—namely, the Reichsanstalt at Berlin—seized the opportunity offered to him as President of the Association at Ipswich to insist, with the authority not only of the head for the time being of a great scientific body, but also of one who himself knew the ways and wants at once of science and of practical life, that the thing which Lodge and others had hoped for was a thing which could be done, and ought to be done at once. And now to-day we can say it has been done. The National Physical Laboratory has been founded. The Address at Ipswich marked the beginning of an organised effort which has at last been crowned with success. A feeling of sadness cannot but come over us when we think that Sir Douglas Galton was not spared to see the formal completion of the scheme whose birth he did so much to help, and which, to his last days, he aided in more ways than one. It is the old story—the good which men do lives after them.

Still older than the Association is this nineteenth century, now swiftly drawing to its close. Though the century itself has yet some sixteen months to run, this is the last meeting of the British Association which will use the numbers eighteen hundred to mark its date.

The eyes of the young look ever forward; they take little heed of the short though ever-lengthening fragment of life which lies behind them; they are wholly bent on that which is to come. The eyes of the aged turn wistfully again and again to the past; as the old glide down the inevitable slope their present becomes a living over again the life which has gone before, and the future takes on the shape of a brief lengthening of the past. May I this evening venture to give rein to the impulses of advancing years? May I, at this last meeting of the Association in the eighteen hundreds, dare to dwell for a while upon the past, and to call to mind a few of the changes which have taken place in the world since those autumn days in which men were saying to each other that the last of the seventeen hundreds was drawing towards its end?

Dover in the year of our Lord seventeen hundred and ninety-nine was in many ways unlike the Dover of to-day. On moonless nights men groped their way in its narrow streets by the help of swinging lanterns and smoky torches, for no lamps lit the ways. By day the light of the sun struggled into the houses through narrow panes of blurred glass. Though the town then, as now, was one of the chief portals to and from the countries beyond the seas, the means of travel were scanty and dear, available for the most part to the rich alone, and, for all, beset with discomfort and risk. Slow and uncertain was the carriage of goods, and the news of the world outside came to the town—though it from its position learnt more than most towns—tardily, fitfully, and often falsely. The people of Dover sat then much in dimness, if not in darkness, and lived in large measure on themselves. They who study the phenomena of living beings tell us that light is the great stimulus of life, and that the fulness of the life of a being or of any of its members may be measured by the variety, the swiftness, and the certainty of the means by which it is in touch with its surroundings. Judged from this standpoint life at Dover then, as indeed elsewhere, must have fallen far short of the life of to-day.

The same study of living beings, however, teaches us that while from one point of view the environment seems to mould the organism, from another point the organism seems to be master of its environment. Going behind the change of circumstances, we may raise the question, the old question, Was life in its essence worth more then than now? Has there been a real advance?

Let me at once relieve your minds by saying that I propose to leave this question in the main unanswered. It may be, or it may not be, that man's grasp of the beautiful and of the good, if not looser, is not firmer than it was a hundred years ago. It may be, or it may not be, that man is no nearer to absolute truth, to seeing things as they really are, than he was then. I will merely ask you to consider with me for a few minutes how far, and in what ways, man's laying hold of that aspect of or part of

truth which we call natural knowledge, or sometimes science, differed in 1799 from what it is to-day, and whether that change must not be accounted a real advance, a real improvement in man.

I do not propose to weary you by what in my hands would be the rash effort of attempting a survey of all the scientific results of the nineteenth century. It will be enough if for a little while I dwell on some few of the salient features distinguishing the way in which we now-a-days look upon, and during the coming week shall speak of, the works of Nature around us—though those works themselves, save for the slight shifting involved in a secular change, remain exactly the same—from the way in which they were looked upon and might have been spoken of at a gathering of philosophers at Dover in 1799. And I ask your leave to do so.

In the philosophy of the ancients, earth, fire, air, and water were called "the elements." It was thought, and rightly thought, that a knowledge of them and of their attributes was a necessary basis of a knowledge of the ways of Nature. Translated into modern language, a knowledge of these "elements" of old means a knowledge of the composition of the atmosphere, of water, and of all the other things which we call matter, as well as a knowledge of the general properties of gases, liquids, and solids, and of the nature and effects of combustion. Of all these things our knowledge to-day is large and exact, and, though ever enlarging, in some respects complete. When did that knowledge begin to become exact?

To-day the children in our schools know that the air which wraps round the globe is not a single thing, but is made up of two things, oxygen and nitrogen,* mingled together. They know, again, that water is not a single thing, but the product of two things, oxygen and hydrogen, joined together. They know that when the air makes the fire burn and gives the animal life, it is the oxygen in it which does the work. They know that all round them things are undergoing that union with oxygen which we call oxidation, and that oxidation is the ordinary source of heat and light. Let me ask you to picture to yourselves what confusion there would be to-morrow, not only in the discussions at the sectional meetings of our Association, but in the world at large, if it should happen that in the coming night some destroying touch should wither up certain tender structures in all our brains, and wipe out from our memories all traces of the ideas which cluster in our minds around the verbal tokens, oxygen and oxidation. How could any of us, not the so-called man of science alone, but even the man of business and the man of pleasure, go about his ways lacking those ideas? Yet those ideas were in 1799 lacking to all but a few.

Although in the third quarter of the seventeenth century the light of truth about oxidation and combustion had flashed out in the writings of John Mayow; it came as a flash only, and died away as soon as it had come. For the rest of that century, and for the greater part of the next, philosophers stumbled about in darkness, misled for the most of the time by the phantom conception which they called phlogiston. It was not until the end of the third quarter of the eighteenth century that the new light, which has burned steadily ever since, lit up the minds of the men of science. The light came at nearly the same time from England and from France. Rounding off the sharp corners of controversy, and joining, as we may fitly do to-day, the two countries as twin bearers of a common crown, we may say that we owe the truth to Cavendish, to Lavoisier, and Priestley. If it was Priestley who was the first to demonstrate the existence of what we now call oxygen, it is to Lavoisier we owe the true conception of the nature of oxidation and the clear exposition of the full meaning of Priestley's discovery, while the knowledge of the composition of water, the necessary complement of the knowledge of oxygen, came to us through Cavendish, and, we may perhaps add, through Watt.

The date of Priestley's discovery of oxygen is 1774, Lavoisier's classic memoir "On the Nature of the Principle which enters into Combination with Metals during Calcination" appeared in 1775, and Cavendish's paper "On the Composition of Water" did not see the light until 1784.

During the last quarter of the Eighteenth Century this new idea of oxygen and oxidation was struggling into existence. How new was the idea is illustrated by the fact that Lavoisier himself at first spoke of that which he was afterwards, namely in 1778, led to call oxygen, the name by which it has since been known, as "the principle which enters into combination." What difficulties its acceptance met with is illustrated by the fact that Priestley himself refused to the end of his life to grasp the true bearings of the discovery which he had made. In the year 1799 the knowledge of oxygen, of the nature of water and of air, and indeed the true conception of chemical composition and chemical change, was hardly more than beginning to be, and the century had to pass wholly away before the next great chemical idea, which we know by the name of the Atomic Theory of John Dalton, was made known. We have only to read the scientific literature of the time to recognise that a truth which is now not only woven as a master-thread into all our scientific conceptions, but even enters largely into the everyday talk and thoughts of educated people, was a hundred years ago struggling into existence among the philosophers themselves. It was all but absolutely unknown to the large world outside those select few.

If there be one word of science which is writ large on the life of the present time, it is the word "electricity"; it is, I take it, writ larger than any other word. The knowledge which it denotes has carried its practical results far and wide into our daily life, while the theoretical conceptions which it signifies pierce deep into the nature of things. We are to-day proud, and justly proud, both of the material triumphs and of the intellectual gains which it has brought us, and we are full of even larger hopes of it in the future.

At what time did this bright child of the Nineteenth Century have its birth?

He who listened to the small group of philosophers of Dover, who in 1799 might have discoursed of natural knowledge, would perhaps have heard much of electric machines, of electric sparks, of electric fluid, and even of positive and negative electricity; for frictional electricity had long been known and even carefully studied. Probably one or more of the group, dwelling on the observations which Galvani, an Italian, had made known some twenty years before, developed views on the connection of electricity with the phenomena of living bodies. Possibly one of them was exciting the rest by telling how he had just heard that a professor at Pavia, one Volta, had discovered that electricity could be produced not only by rubbing together particular bodies, but by the simple contact of two metals, and had thereby explained Galvani's remarkable results. For, indeed, as we shall hear from Professor Fleming, it was in that very year, 1799, that electricity as we now know it took its birth. It was then that Volta brought to light the apparently simple truths out of which so much has sprung. The world, it is true, had to wait for yet some twenty years before both the practical and the theoretic worth of Volta's discovery became truly pregnant, under the fertilising influence of another discovery. The loadstone and magnetic virtues had, like the electrifying power of rubbed amber, long been an old story. But, save for the compass, not much had come from it. And even Volta's discovery might have long remained relatively barren had it been left to itself. When, however, in 1819, Oersted made known his remarkable observations on the relations of electricity to magnetism,

* Some may already know that there is at least a third thing, argon.

he made the contact needed for the flow of a new current of ideas. And it is perhaps not too much to say that those ideas, developing during the years of the rest of the century with an ever-accelerating swiftness, have wholly changed man's material relations to the circumstances of life, and at the same time carried him far in his knowledge of the nature of things.

Of all the various branches of science, none perhaps is to-day, none for these many years past has been, so well known to, even if not understanded by, most people as that of geology. Its practical lessons have brought wealth to many; its fairy tales have brought delight to more; and round it hovers the charm of danger, for the conclusions to which it leads touch on the nature of man's beginning.

In 1799, the science of geology, as we now know it, was struggling into birth. There had been from of old cosmogonies, theories as to how the world had taken shape out of primæval chaos. In that fresh spirit which marked the zealous search after natural knowledge pursued in the middle and latter part of the Seventeenth Century, the brilliant Stenson, in Italy, and Hooke, in our own country, had laid hold of some of the problems presented by fossil remains, and Woodward, with others, had laboured in the same field. In the Eighteenth Century, especially in its latter half, men's minds were busy about the physical agencies determining or modifying the features of the earth's crust; water and fire, subsidence from a primæval ocean and transformation by outbursts of the central heat, Neptune and Pluto, were being appealed to, by Werner on the one hand, and by Desmarest on the other, in explanation of the earth's phenomenon. The way was being prepared, theories and views were abundant, and many sound observations had been made; and yet the science of geology, properly so-called, the exact and proved knowledge of the successive phases of the world's life, may be said to date from the closing years of the Eighteenth Century.

In 1783, James Hutton put forward in a brief memoir his "Theory of the Earth," which in 1795, two years before his death, he expanded into a book; but his ideas failed to lay hold of men's minds until the century had passed away, when, in 1802, they found an able expositor in John Playfair. The very same year that Hutton published his theory, Cuvier came to Paris and almost forthwith began, with Brongniart, his immortal researches into the fossils of Paris and its neighbourhood. And four years later, in the year 1799 itself, William Smith's tabular list of strata and fossils saw the light. It is, I believe, not too much to say that out of these geology, as we now know it, has sprung. It was thus in the closing years of the Eighteenth Century that was began the work which the Nineteenth Century has carried forward to such great results. But at that time only the select few had grasped the truth, and even they only the beginning of it. Outside a narrow circle the thoughts, even of the educated, about the history of the globe, were bounded by the story of the Deluge—though the story was often told in a strange fashion—or were guided by the fantastic views of the plastic forces of a sportive Nature.

In another branch of science, in that which deals with the problems presented by living beings, the thoughts of men in 1779 were also very different from the thoughts of men to-day. It is a very old quest, the quest after the knowledge of the nature of living beings, one of the earliest on which man set out; for it promised to lead him to a knowledge of himself, a promise which perhaps is still before us, but the fulfilment of which is as yet far off. As time has gone on, the pursuit of natural knowledge has seemed to lead man away from himself into the furthermost parts of the universe, and into secret workings of Nature in which he appears to be of little or no account; and his knowledge of the nature of living things, and so of his own nature, has advanced slowly, waiting till the progress of other branches of natural knowledge can bring it aid. Yet in the past hundred years, the biologic sciences, as we now call them, have marched rapidly onward.

We may look upon a living body as a machine doing work in accordance with certain laws, and may seek to trace out the working of the inner wheels, how these raise up the lifeless dust into living matter, and let the living matter fall away again into dust, giving out movement and heat. Or we may look upon the individual life as a link in a long chain, joining something which went before to something about to come, a chain whose beginning lies hid in the farthest past, and may seek to know the ties which bind one life to another. As we call up to view the long series of living forms, living now or flitting like shadows on the screen of the past, we may strive to lay hold of the influences which fashion the garment of life. Whether the problems of life are looked upon from the one point of view or the other, we to-day, not biologists only, but all of us, have gained a knowledge hidden even from the philosophers a hundred years ago.

Of the problems presented by the living body viewed as a machine, some may be spoken of as mechanical, others as physical, and yet others as chemical, while some are, apparently at least, none of these. In the Seventeenth Century, William Harvey, laying hold of the central mechanism of the blood stream, opened up a path of inquiry which his own age and the century which followed trod with marked success. The knowledge of the mechanics of the animal and of the plant advanced apace; but the physical and chemical problems had yet to wait. The Eighteenth Century, it is true, had its physics and its chemistry; but, in relation at least to the problems of the living being, a chemistry which knew not oxygen and a physics which knew not the electricity of chemical action were of little avail. The philosopher of 1799, when he discussed the functions of the animal or of the plant involving chemical changes, was fain for the most part, as were his predecessors in the century before, to have recourse to such vague terms as "fermentation" and the like; to-day our treatises on physiology are largely made up of precise and exact expositions of the play of physical agencies and chemical bodies in the living organism. He made use of the words "vital force" or "vital principle" not as an occasional, but as a common, explanation of the phenomena of the living body. During the present century, especially during its latter half, the idea embodied in those words has been driven away from one seat after another; if we use it now when we are dealing with the chemical and physical events of life we use it with reluctance, as a *deus ex machina* to be appealed to only when everything else has failed.

Some of the problems—and those, perhaps, the chief problems—of the living body have to be solved neither by physical nor by chemical methods, but by methods of their own. Such are the problems of the nervous system. In respect of these the men of 1799 were on the threshold of a pregnant discovery. During the latter part of the present century, and especially during its last quarter, the analysis of the mysterious processes in the nervous system, and especially in the brain, which issue as feeling, thought, and the power to move, has been pushed forward with a success conspicuous in its practical, and full of promise in its theoretical, gains. That analysis may be briefly described as a following up of threads. We now know that what takes place along a tiny thread which we call a nerve-fibre differs from that which takes place along its fellow threads, that differing nervous impulses travel along different nerve fibres, and that nervous and psychical events are the outcome of the clashing of nervous impulses as they sweep along the closely-woven web of living threads of which the brain is made. We have learnt by experiment and by observation that the pattern of the web determines the play of the impulses, and we can already explain many of the obscure problems not only of nervous disease, but of nervous life, by an analysis which

is a tracking out the devious and linked paths of nervous threads. The very beginning of this analysis was unknown in 1799. Men knew that nerves were the agents of feeling and of the movements of muscles; they had learnt much about what this part or that part of the brain could do; but they did not know that one nerve-fibre differed from another in the very essence of its work. It was just about the end of the past century, or the beginning of the present one, that an English surgeon began to ponder over a conception which, however, he did not make known until some years later, and which did not gain complete demonstration and full acceptance until still more years had passed away. It was in 1811, in a tiny pamphlet published privately, that Charles Bell put forward his "New Idea" that the nervous system was constructed on the principle that "the nerves are not single nerves possessing various powers, but bundles of different nerves, whose filaments are united for the convenience of distribution, but which are distinct in office as they are in origin from the brain."

Our present knowledge of the nervous system is to a large extent only an exemplification and expansion of Charles Bell's "New Idea," and has its origin in that.

If we pass from the problems of the living organism viewed as a machine to those presented by the varied features of the different creatures who have lived, or who still live on the earth, we at once call to mind that the middle years of the present century mark an epoch in biologic thought such as never came before, for it was then that Charles Darwin gave to the world the "Origin of Species."

That work, however, with all the far-reaching effects which it has had, could have had little or no effect, or, rather, could not have come into existence, had not the earlier half of the century been in travail preparing for its coming. For the germinal idea of Darwin appeals, as to witnesses, to the results of two lines of biologic investigation which were almost unknown to the men of the Eighteenth Century.

To one of these lines I have already referred. Darwin, as we know, appealed to the geological record; and we also know how that record, imperfect as it was then, and imperfect as it must always remain, has since his time yielded the most striking proofs of at least one part of his general conception. In 1799 there was, as we have seen, no geological record at all.

Of the other line I must say a few words.

To-day the merest beginner in biologic study, or even that exemplar of acquaintance without knowledge, the general reader, is aware that every living being, even man himself, begins its independent existence as a tiny ball, of which we can, even acknowledging to the full the limits of the optical analysis at our command, assert with confidence that in structure, using that word in its ordinary sense, it is in all cases absolutely simple. It is equally well known that the features of form which supply the characters of a grown-up living being, all the many and varied features of even the most complex organism, are reached as the goal of a road, at times a long road, of successive changes; that the life of every being, from the ovum to its full estate, is a series of shifting scenes, which come and go, sometimes changing abruptly, sometimes melting the one into the other, like dissolving views, all so ordained that often the final shape with which the creature seems to begin, or is said to begin, its life in the world is the outcome of many shapes, clothed with which it in turn has lived many lives before its seeming birth.

All or nearly all the exact knowledge of the laboured way in which each living creature puts on its proper shape and structure is the heritage of the present century. Although the way in which the chick is moulded in the egg was not wholly unknown even to the ancients, and in later years had been told, first in the Sixteenth Century by Fabricius, then in the Seventeenth Century in a more clear and striking manner by the great Italian naturalist Malpighi, the teaching thus offered had been neglected or misinterpreted. At the close of the Eighteenth Century the dominant view was that in the making of a creature out of the egg there was no putting on of wholly new parts, no epigenesis. It was taught that the entire creature lay hidden in the egg, hidden by reason of the very transparency of its substance, lay ready-made but folded up, as it were, and that the process of development within the egg or within the womb was a mere unfolding, a simple evolution. Nor did men shrink from accepting the logical outcome of such a view—namely, that within the unborn creature itself lay in like manner, hidden and folded up, its offspring also, and within that again its offspring in turn, after the fashion of a cluster of ivory balls carved by Chinese hands, one within the other. This was no fantastic view put forward by an imaginative dreamer; it was seriously held by sober men, even by men like the illustrious Haller, in spite of their recognising that as the chick grew in the egg some changes of form took place. Though so early as the middle of the Eighteenth Century Friedrich Caspar Wolff and, later on, others had strenuously opposed such a view, it held its own not only to the close of the century, but far on into the next. It was not until a quarter of the present century had been added to the past that Von Baer made known the results of researches which once and for all swept away the old view. He and others working after him made it clear that each individual puts on its final form and structure not by an unfolding of pre-existing hidden features, but by the formation of new parts through the continued differentiation of a primitively simple material. It was also made clear that the successive changes which the embryo undergoes in its progress from the ovum to maturity are the expression of morphologic laws, that the progress is one from the general to the special, and that the shifting scenes of embryonic life are hints and tokens of lives lived by ancestors in times long past.

If we wish to measure how far off in biologic thought the end of the last century stands, not only from the end, but even from the middle of this one, we may imagine Darwin striving to write the "Origin of Species" in 1799. We may fancy him being told by philosophers explaining how one group of living beings differed from another group, because all its members and all their ancestors came into existence at one stroke when the first-born progenitor of the race, within which all the rest were folded up, stood forth as the result of a creative act. We may fancy him listening to a debate between the philosopher who maintained that all the fossils strewn in the earth were the remains of animals or plants churned up in the turmoil of a violent universal flood, and dropped in their places as the waters went away, and him who argued that such were not really the "spoils of living creatures," but the products of some playful plastic power, which out of the superabundance of its energy fashioned here and there the lifeless earth into forms which imitated, but only imitated, those of living things. Could he amid such surroundings by any flight of genius have beat his way to the conception for which his name will ever be known?

Here I may well turn away from the past. It is not my purpose, nor, as I have said, am I fitted, nor is this perhaps the place, to tell even in outline the tale of the work of science in the Nineteenth Century. I am content to have pointed out that the two great sciences of chemistry and geology took their birth, or at least began to stand alone, at the close of the last century, and have grown to be what we know them now within about a hundred years, and that the study of living beings has within the same time been so transformed as to be to-day something wholly different from what it was in 1799. And, indeed, to say more would be to repeat almost the same story about other things. If our present knowledge of electricity is essentially the child of the Nineteenth Century, so also is our present knowledge of many other branches of physics. And those most ancient forms of exact knowledge, the

knowledge of numbers and of the heavens, whose beginning is lost in the remote past, have, with all other kinds of natural knowledge, moved onward during the whole of the hundred years with a speed which is ever increasing. I have said, I trust, enough to justify the statement that in respect to natural knowledge a great gulf lies between 1799 and 1899. That gulf, moreover, is a two-fold one: not only has natural knowledge been increased, but men have run to and fro spreading it as they go. Not only have the few driven far back round the full circle of natural knowledge the dark clouds of the unknown which wrap us all about, but also the many walk in the zone of light thus increasingly gained. If it be true that the few to-day are, in respect to natural knowledge, far removed from the few of those days, it is also true that nearly all which the few alone knew then, and much which they did not know, has now become the common knowledge of the many.

What, however, I may venture to insist upon here is that the difference in respect to natural knowledge, whatever be the case with other differences between then and now, is undoubtedly a difference which means progress. The span between the science of that time and the science of to-day is beyond all question a great stride onwards.

We may say this, but we must say it without boasting. For the very story of the past which tells of the triumphs of science bids the man of science put away from him all thoughts of vainglory. And that by many tokens.

Whoever, working at any scientific problem, has occasion to study the inquiries into the same problem made by some fellow-worker in the years long gone by, comes away from that study humbled by one or other of two different thoughts. On the one hand he may find, when he has translated the language of the past into the phraseology of to-day, how near was his forerunner of old to the conception which he thought, with pride, was all his own, not only so true but so new. On the other hand, if the ideas of the investigator of old, viewed in the light of modern knowledge, are found to be so wide of the mark as to seem absurd, the smile which begins to play upon the lips of the modern is checked by the thought, Will the ideas which I am now putting forth, and which I think explain so clearly, so fully, the problem in hand, seem to some worker in the far future as wrong and as fantastic as do these of my forerunner to me? In either case his personal pride is checked. Further, there is written clearly on each page of the history of science, in characters which cannot be overlooked, the lesson that no scientific truth is born anew, coming by itself and of itself. Each new truth is always the offspring of something which has gone before, becoming in turn the parent of something coming after. In this aspect the man of science is unlike, or seems to be unlike, the poet and the artist. The poet is born, not made; he rises up, no man knowing his beginnings; when he goes away, though men after him may sing his songs for centuries, he himself goes away wholly, having taken with him his mantle, for this he can give to none other. The man of science is not thus creative; he is created. His work, however great it be, is not wholly his own; it is in part the outcome of the work of men who have gone before. Again and again a conception which has made a name great has come not so much by the man's own effort as out of the fulness of time. Again and again we may read in the words of some man of old the outlines of an idea which in later days has shone forth as a great acknowledged truth. From the mouth of the man of old the idea dropped barren, fruitless; the world was not ready for it, and heeded it not; the concomitant and abutting truths which could give it power to work were wanting. Coming back again in later days, the same idea found the world awaiting it; things were in travail preparing for it; and someone, seizing the right moment to put it forth again, leapt into fame. It is not so much the men of science who make science, as some spirit which, born of the truths already won, drives the man of science onward, and uses him to win new truths in turn.

It is because each man of science is not his own master, but one of many obedient servants of an impulse which was at work long before him, and will work long after him, that in science there is no falling back. In respect to other things there may be times of darkness and times of light; there may be risings, decadences, and revivals. In science there is only progress. The path may not be always a straight line, there may be swerving to this side and to that, ideas may seem to return again and again to the same point of the intellectual compass; but it will always be found that they have reached a higher level—they have moved, not in a circle, but in a spiral. Moreover science is not fashioned as is a house, by putting brick to brick, that which is once put remaining as it was put to the end. The growth of science is that of a living being. As in the embryo phase follows phase, and each member of the body puts on in succession different appearances, though all the while the same member, so a scientific conception of one age seems to differ from that of a following age, though it is the same one in the process of being made; and as the dim outlines of the early embryo become, as the being grows more distinct and sharp, like a picture on a screen brought more and more into focus, so the dim gropings and searchings of the men of science of old are by repeated approximations wrought into the clear and exact conclusions of later times.

The story of natural knowledge, of science, in the nineteenth century, as, indeed, in preceding centuries, is, I repeat, a story of continued progress. There is in it not so much as a hint of falling back, not even of standing still. What is gained by scientific inquiry is gained for ever; it may be added to, it may seem to be covered up, but it can never be taken away. Confident that the progress will go on, we cannot help peering into the years to come and straining our eyes to foresee what science will become and what it will do as they roll on. While we do so, the thought must come to us, Will all the increasing knowledge of Nature avail only to change the ways of man—will it have no effect on man himself?

The material good which mankind has gained and is gaining through the advance of science is so imposing as to be obvious to everyone, and the praises of this aspect of science are to be found in the mouths of all. Beyond all doubt science has greatly lessened and has markedly narrowed hardship and suffering; beyond all doubt science has largely increased and has widely diffused ease and comfort. The appliances of science have, as it were, covered with a soft cushion the rough places of life, and that not for the rich only, but also for the poor. So abundant and so prominent are the material benefits of science that in the eyes of many these seem to be the only benefits which she brings. She is often spoken of as if she were useful and nothing more, as if her work were only to administer to the material wants of man.

Is this so?

We may begin to doubt it when we reflect that the triumphs of science which bring these material advantages are in their very nature intellectual triumphs. The increasing benefits brought by science are the results of man's increasing mastery over Nature, and that mastery is increasingly a mastery of mind; it is an increasing power to use the forces of what we call inanimate nature in place of the force of his own or other creatures' bodies; it is an increasing use of mind in place of muscle.

Is it to be thought that that which has brought the mind so greatly into play has had no effect on the mind itself? Is that part of the mind which works out scientific truths a mere slavish machine, producing results it knows not how, having no part in the good which in its working it brings forth;

What are the qualities, the features of that scientific

mind which has wrought, and is working, such great changes in man's relation to Nature? In seeking an answer to this question we have not to inquire into the attributes of genius. Though much of the progress of science seems to take on the form of a series of great steps, each made by some great man, the distinction in science between the great discoverer and the humble worker is one of degree only, not of kind. As I was urging just now, the greatness of many great names in science is often, in large part, the greatness of occasion, not of absolute power. The qualities which guide one man to a small truth silently taking its place among its fellows, as these go to make up progress, are at bottom the same as those by which another man is led to something of which the whole world rings.

The features of the fruitful scientific mind are in the main three.

In the first place, above all other things, his nature must be one which vibrates in unison with that of which he is in search; the seeker after truth must himself be truthful, truthful with the truthfulness of Nature. For the truthfulness of Nature is not wholly the same as that which man sometimes calls truthfulness. It is far more imperious, far more exacting. Man, unscientific man, is often content with "the nearly" and "the almost." Nature never is. It is not her way to call the same two things which differ, though the difference may be measured by less than the thousandth of a milligramme or of a millimetre, or by any other like standard of minuteness. And the man who, carrying the ways of the world into the domain of science, thinks that he may treat Nature's differences in any other way than she treats them herself, will find that she resents his conduct; if he in carelessness or in disdain overlooks the minute difference which she holds out to him as a signal to guide him in his search, the projecting tip, as it were, of some buried treasure, he is bound to go astray, and the more strenuous he struggles on, the farther will he find himself from his true goal.

In the second place, he must be alert of mind. Nature is ever making signs to us, she is ever whispering to us the beginnings of her secrets; the scientific man must be ever on the watch, ready at once to lay hold of Nature's hint however small, to listen to her whisper however low.

In the third place, scientific inquiry, though it be preeminently an intellectual effort, has need of the moral quality of courage—not so much the courage which helps a man to face a sudden difficulty as the courage of steadfast endurance. Almost every inquiry, certainly every prolonged inquiry, sooner or later goes wrong. The path, at first so straight and clear, grows crooked and gets blocked; the hope and enthusiasm, or even the jaunty ease, with which the inquirer set out, leave him, and he falls into a slough of despond. That is the critical moment calling for courage. Struggling through the slough he will find on the other side of the wicket-gate opening up the real path; losing heart he will turn back and add one more stone to the great cairn of the unaccomplished.

But, I hear some one say, these qualities are not the peculiar attributes of the man of science; they may be recognised as belonging to almost everyone who has commanded or deserved success, whatever may have been his walk of life. That is so. That is exactly what I would desire to insist, that the men of science have no peculiar virtues, no special powers. They are ordinary men, their characters are common, even commonplace. Science, as Huxley said, is organised common sense, and men of science are common men, drilled in the ways of common sense.

For their life has this feature. Though in themselves they are no stronger, no better than other men, they possess a strength which, as I have just now urged, is not their own, but is that of the science whose servants they are. Even in his apprenticeship the scientific inquirer, while learning what has been done before his time, if he learns it aright, so learns it that what is known may serve him not only as a vantage ground whence to push off into the unknown, but also as a compass to guide him in his course. And when fitted for his work he enters on inquiry itself, what a zealous anxious guide, what a strict and—because strict—helpful school-mistress does Nature make herself to him! Under her care every inquiry, whether it bring the inquirer to a happy issue or seem to end in nought, trains him for the next effort. She so orders her ways that each act of obedience to her makes the next act easier for him, and step by step she leads him on towards that perfect obedience which is complete mastery.

Indeed, when we reflect on the potency of the discipline of scientific inquiry, we cease to wonder at the progress of scientific knowledge. The results actually gained seem to fall so far short of what under such guidance might have been expected to have been gathered in that we are fain to conclude that science has called to follow her, for the most part, the poor in intellect and the wayward in spirit. Had she called to her service the many acute minds who have wasted their strength struggling in vain to solve hopeless problems, or who have turned their energies to things other than the increase of knowledge; had she called to her service the many just men who have walked straight without the need of a rod to guide them, how much greater than it has been would have been the progress of science, and how many false teachings would the world have been spared! To men of science themselves, when they consider their favoured lot, the achievements of the past should serve not as a boast, but as a reproach.

If there be any truth in what I have been urging, that the pursuit of scientific inquiry is itself a training of special potency, giving strength to the feeble and keeping in the path those who are inclined to stray, it is obvious that the material gains of science, great as they may be, do not make up all the good which science brings or may bring to man. We especially, perhaps, in these later days, through the rapid development of the physical sciences, are too apt to dwell on the material gains alone. As a child in its infancy looks upon its mother only as a giver of good things, and does not learn till in after days how she was also showing her love by carefully training it in the way it should go, so we, too, have thought too much of the gifts of science, overlooking her power to guide.

Man does not live by bread alone, and science brings him more than bread. It is a great thing to make two blades of grass grow where before one alone grew; but it is no less great a thing to help a man to come to a just conclusion on the questions with which he has to deal. We may claim for science that while she is doing the one she may be so used as to do the other also. The dictum just quoted, that science is organised common sense, may be read as meaning that the common problems of life which common people have to solve are to be solved by the same methods by which the man of science solves his special problems. It follows that the training which does so much for him may be looked to as promising to do much for them. Such aid can come from science on two conditions only. In the first place, this her influence must be acknowledged; she must be duly recognised as a teacher no less than as a hewer of wood and a drawer of water. And the pursuit of science must be followed not by the professional few only, but, at least in such measure as will ensure the influence of example, by the many. But this latter point I need not urge before this great Association, whose chief object during more than half a century has been to bring within the fold of science all who would answer to the call. In the second place, it must be understood that the training to be looked for from science is the outcome not of the accumulation of scientific knowledge, but of the practice of scientific inquiry. Man may have at his fingers' ends all the accomplished results and all the current opinions of any one

or of all the branches of science, and yet remain wholly unscientific in mind; but no one can have carried out even the humblest research without the spirit of science in some measure resting upon him. And that spirit may in part be caught even without entering upon an actual investigation in search of a new truth. The learner may be led to old truths, even the oldest, in more ways than one. He may be brought abruptly to a truth in its finished form, coming straight to it like a thief climbing over the wall; and the hurry and press of modern life tempt many to adopt this quicker way. Or he may be more slowly guided along the path by which the truth was reached by him who first laid hold of it. It is by this latter way of learning the truth, and by this alone, that the learner may hope to catch something at least of the spirit of the scientific inquirer.

This is not the place, nor have I the wish, to plunge into the turmoil of controversy; but, if there be any truth in what I have been urging, then they are wrong who think that in the schooling of the young science can be used with profit only to train those for whom science will be the means of earning their bread. It may be that from the point of view of the pedagogic art the experience of generations has fashioned out of the older studies of literature an instrument of discipline of unusual power, and that the teaching of science is as yet but a rough tool in unpractised hands. That, however, is not an adequate reason why scope should not be given for science to show the value which we claim for it as an intellectual training fitted for all sorts and conditions of men. Nor need the studies of humanity and literature fear her presence in the schools, for if her friends maintain that that teaching is one-sided, and therefore misleading, which deals with the doings of man only, and is silent about the works of Nature, in the sight of which he and his doings shrink almost to nothing, she herself would be the first to admit that that teaching is equally wrong which deals only with the works of Nature and says nothing about the doings of man, who is, to us at least, Nature's centre.

There is yet another general aspect of science on which I would crave leave to say a word. In that broad field of human life which we call politics, in the struggle not of man with man, but of race with race, science works for good. If we look only on the surface it may at first sight seem otherwise. In no branch of science has there during these later years been greater activity and more rapid progress than in that which furnishes the means by which man brings death, suffering, and disaster on his fellow-men. If the healer can look with pride on the increased power which science has given him to alleviate human suffering and ward off the miseries of disease, the destroyer can look with still greater pride on the power which science has given him to sweep away lives and to work desolation and ruin; while the one has slowly been learning to save units, the other has quickly learnt to slay thousands. But, happily, the very greatness of the modern power of destruction is already becoming a bar to its use, and bids fair—may we hope before long?—wholly to put an end to it; in the words of Tacitus, though in another sense, the very preparations for war, through the character which science gives them, make for peace.

Moreover, not in one branch of science only, but in all, there is a deep undercurrent of influence sapping the very foundations of all war. As I have already urged, no feature of scientific inquiry is more marked than the dependence of each step forward on other steps which have been made before. The man of science cannot sit by himself in his own cave weaving out results by his own efforts, unaided by others, heedless of what others have done and are doing. He is but a bit of a great system, a joint in a great machine, and he can only work aright when he is in due touch with his fellow-workers. If his labour is to be what it ought to be, and is to have the weight which it ought to have, he must know what is being done, not by himself, but by others, and by others not of his own land and speaking his tongue only, but also of other lands and of other speech. Hence it comes about that to the man of science the barriers of manners and of speech which pen men into nations become more and more unreal and indistinct. He recognises his fellow-worker, wherever he may live and whatever tongue he may speak, as one who is pushing forward shoulder to shoulder with him towards a common goal, as one whom he is helping and who is helping him. The touch of science makes the whole world kin.

The history of the past gives us many examples of this brotherhood of science. In the revival of learning throughout the Sixteenth and Seventeenth Centuries, and some way on into the Eighteenth Century, the common use of the Latin tongue made intercourse easy. In some respects in those earlier days science was more cosmopolitan than it afterwards became. In spite of the difficulties and hardships of travel, the men of science of different lands again and again met each other face to face, heard with their ears, and saw with their eyes what their brethren had to say or to show. The Englishman took the long journey to Italy to study there; the Italian, the Frenchman, and the German wandered from one seat of learning to another; and many a man held a chair in a country not his own. There was help, too, as well as intercourse. The Royal Society of London took upon itself the task of publishing nearly all the works of the great Italian Malpighi, and the brilliant Lavoisier, two years before his own countrymen in their blind fury slew him, received from the same body the highest token which it could give of its esteem.

In these closing years of the Nineteenth Century this great need of mutual knowledge and of common action felt by men of science of different lands is being manifested in a special way. Though now-a-days what is done anywhere is soon known everywhere, the news of a discovery being often flashed over the globe by telegraph, there is an increasing activity in the direction of organisation to promote international meetings and international co-operation. In almost every science inquirers from many lands now gather together at stated intervals in international congresses to discuss matters which they have in common at heart and go away, each one feeling strengthened by having met his brother. The desire that in the struggle to lay bare the secrets of Nature the least waste of human energy should be incurred is leading more and more to the concerted action of nations combining to attack problems, the solution of which is difficult and costly. The determination of standards of measurement, magnetic surveys, the solution of great geodetic problems, the mapping of the heavens and of the earth—all these are being carried on by international organisations.

In this and in other countries men's minds have this long while past been greatly moved by the desire to make fresh efforts to pierce the dark secrets of the forbidding Antarctic regions. Belgium has just made a brave single-handed attempt; a private enterprise sailing from these shores is struggling there now, lost for the present to our view; and this year we in England and our brethren in Germany are, thanks to the promised aid of the respective Governments, and no less to private liberality, in which this Association takes it share, able to begin the preparation of carefully organised expeditions. That international amity of which I am speaking is illustrated by the fact that in this country, and in that there is not only a great desire, but a firm purpose, to secure the fullest co-operation between the expeditions which will leave the two shores. If in this momentous attempt any rivalry be shown between the two nations, it will be for each a rivalry, not in forestalling, but in assisting the other. May I add that if the story of the past may seem to give our nation some claim to the seas as more peculiarly our own, that claim bespeaks a duty likewise peculiarly our own to leave no effort untried by which we may plumb the seas' yet unknown depths, and trace their yet unknown shores? That claim, if it means anything, means that when nations are

joining hands in the dangerous work of exploring the unknown South, the larger burden of the task should fall to Britain's share; it means that we in this country should see to it, and see to it at once, that the concerted Antarctic expedition which in some two years or so will leave the shores of Germany, of England, and, perhaps, of other lands, should, so far as we are concerned, be so equipped and so sustained that the risk of failure and disaster may be made as small, and the hope of being able not merely to snatch a hurried glimpse of lands not yet seen, but to gather in with full hands a rich harvest of the facts which men not of one science only, but of many, long to know, as great as possible.

Another international scientific effort demands a word of notice. The need which every inquirer in science feels to know, and to know quickly, what his fellow-worker, wherever on the globe he may be carrying on his work or making known his results, has done or is doing, led some four years back to a proposal for carrying out by international co-operation a complete current index, issued promptly, of the scientific literature of the world. Though much labour in many lands has been spent upon the undertaking, the project is not yet an accomplished fact. Nor can this, perhaps, be wondered at, when the difficulties of the task are weighed. Difficulties of language, difficulties of driving in one team all the several sciences which, like young horses, wish each to have its head free with leave to go its own way, difficulties mechanical and financial of press and post, difficulties raised by existing interests—these and yet other difficulties are obstacles not easy to be overcome. The most striking and the most encouraging features of the deliberations which have now been going on for three years have been the repeated expressions, coming not from this or that quarter only, but from almost all quarters, of an earnest desire that the effort should succeed, of a sincere belief in the good of international co-operation, and of a willingness to sink as far as possible individual interests for the sake of the common cause. In the face of such a spirit we may surely hope that the many difficulties will ultimately pass out of sight.

Perhaps, however, not the least notable fact of international co-operation in science is the proposal which has been made within the last two years that the leading academies of the world should, by representatives, meet at intervals to discuss questions in which the learned of all lands are interested. A month hence a preliminary meeting of this kind will be held at Wiesbaden; and it is at least probable that the closing year of that Nineteenth Century in which science has played so great a part may, at Paris during the great World's Fair—which every friend, not of science only, but of humanity, trusts may not be put aside or even injured through any untoward event, and which promises to be an occasion not of pleasurable sight-seeing only, but also, by its many international congresses, of international communing in the search for truth—witness the first select Witenagemote of the science of the world.

I make no apology for having thus touched on international co-operation. I should have been wanting, had I not done so, to the memorable occasion of this meeting. A hundred years ago two great nations were grappling with each other in a fierce struggle, which had lasted, with pauses, for many years, and was to last for many years to come; war was on every lip and in almost every heart. To-day this meeting has, by a common wish, been so arranged that those two nations should, in the persons of their men of science, draw as near together as they can, with nothing but the narrow streak of the Channel between them, in order that they may take counsel together on matters in which they have one interest and a common hope. May we not look upon this brotherly meeting as one of many signs that science, though she works in a silent manner and in ways unseen by many, is steadily making for peace?

Looking back, then, in this last year of the eighteen hundreds, on the century which is drawing to its close, while we may see in the history of scientific inquiry much which, telling the man of science of his short-comings and his weakness, bids him be humble, we also see much, perhaps more, which gives him hope. Hope is indeed one of the watchwords of science. In the latter-day writings of some who know not science, much may be read which shows that the writer is losing or has lost hope in the future of mankind. There are not a few of these; their repeated utterances make a sign of the times. Seeing in matters lying outside science few marks of progress and many tokens of decline or of decay, recognising in science its material benefits only, such men have thoughts of despair when they look forward to the times to come. But if there be any truth in what I have attempted to urge to-night, if the intellectual, if the moral influences of science are no less marked than her material benefits, if, moreover, that which she has done is but the earnest of that which she shall do, such men may pluck up courage and gather strength by laying hold of her garment. We men of science at least need not share their views or their fears. Our feet are set, not on the shifting sands of the opinions and of the fancies of the day, but on a solid foundation of verified truth, which by the labours of each succeeding age is made broader and more firm. To us the past is a thing to look back upon, not with regret, not as something which has been lost never to be regained, but with content, as something whose influence is with us still, helping us on our further way. With us, indeed, the past points not to itself, but to the future; the golden age is in front of us, not behind us; that which we do know is a lamp whose brightest beams are shed into the unknown before us, showing us how much there is in front and lighting up the way to reach it. We are confident in the advance because, as each one of us feels that any step forward which he may make is not ordered by himself alone, and is not the result of his own sole efforts in the present, but is, and that in large measure, the outcome of the labours of others in the past, so each one of us has the sure and certain hope that as the past has helped him, so his efforts, be they great or be they small, will be a help to those to come.

SOLID HYDROGEN.*

By JAMES DEWAR, F.R.S., &c.

In the autumn of 1898, after the production of liquid hydrogen was possible on a scale of one or two hundred c.c., its solidification was attempted under reduced pressure. At this time, to make the isolation of the hydrogen as effective as possible, the hydrogen was placed in a small vacuum test-tube, placed in a larger vessel of the same kind. Excess of the hydrogen partly filled the circular space between the two vacuum vessels. The apparatus is shown in Fig. 1. In this way the evaporation was mainly thrown on the liquid hydrogen in the annular space between the tubes. In this arrangement the outside surface of the smaller tube was kept at the same temperature as the inside, so that the liquid hydrogen for the time was effectually guarded from influx of heat. With such a combination the liquid hydrogen was evaporated under some 10 m.m. pressure, yet no solidification took place. Seeing experiments of this kind required a large supply of the liquid; other problems were attacked, and any attempts in the direction of producing the solid for the time abandoned. During the course of the present year many varieties of electric resistance thermometers have been under observation, and with some of these the reduction of temperature brought about by exhaustion was investigated. Thermometers constructed

*Read before the British Association (Section B), Dover Meeting, 1899.

of platinum and platinum-rhodium (alloy) were only lowered 1½° C. by exhaustion of the liquid hydrogen, and they all gave a boiling-point of −245° C., whereas the reduction in temperature by evaporation *in vacuo* ought to be 5° C., and the true boiling-point from −252° to −253° C. In the course of these experiments it was noted that almost invariably there was a slight leak of air, which became apparent by its being frozen into an air snow in the interior of the vessel, where it met the cold vapour of hydrogen coming off. When conducting wires covered with silk have to pass through india-rubber corks it is very difficult at these excessively low temperatures to prevent leaks, when corks get as hard as a stone, and cements crack in all directions. The effect of this slight air leak on the liquid hydrogen when the pressure got reduced below 60 m.m. was very remarkable, as it suddenly solidified into a white froth-like mass like frozen foam. My first impressions were that this body was a sponge of solid air containing the liquid hydrogen, just like ordinary air, which is a magma of solid nitrogen containing liquid oxygen. The fact, however, that this white solid froth evaporated completely at the low pressure without leaving any substantial amount of solid air led to the conclusion that the body after all must be solid hydrogen. This surmise was confirmed by observing that if the pressure, and therefore the temperature, of the hydrogen was allowed to rise, the solid melted when the pressure reached about 55 m.m.

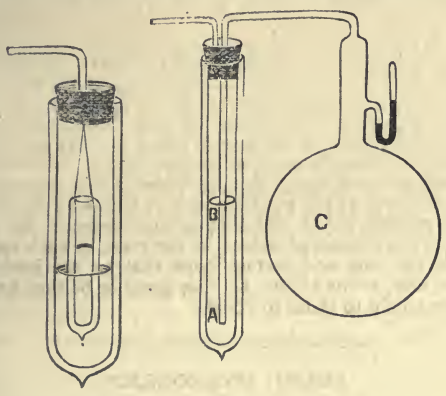

FIG 1.

FIG 2.

The failure of the early experiment must then have been due to supercooling of the liquid, which is prevented in this case by contact with metallic wires and traces of solid air. To settle the matter definitely the following experiment was arranged. A flask C of about a litre capacity, to which a long glass tube bent twice at right angles was sealed, as shown in Fig. 2, and to which a small mercury manometer can be sealed, was filled with pure dry hydrogen and sealed off. The lower portion AB of this tube was calibrated. It was surrounded with liquid hydrogen placed in a vacuum vessel arranged for exhaustion. As soon as the pressure got well reduced below that of the atmosphere, perfectly clear liquid hydrogen began to collect in the tube AB, and could be observed accumulating until, about 30 to 40 m.m. pressure, the liquid hydrogen surrounding the outside of the tube suddenly passed into a solid white foam-like mass, almost filling the whole space. As it was not possible to see the condition of the hydrogen in the interior of the tube AB when it was covered with a large quantity of this solid, the whole apparatus was turned upside down in order to see whether any liquid would run down AB into the flask C. Liquid did not flow down the tube, so the liquid hydrogen with which the tube was partly filled must have solidified. By placing a strong light on the side of the vacuum test-tube opposite the eye, and maintaining the exhaustion to about 25 m.m., gradually the solid became less opaque, and the material in AB was seen to be a transparent ice in the lower part, but the surface looked frothy. This fact prevented the solid density from being determined, but the maximum fluid density has been approximately ascertained. This was found to be 0·086, the liquid at its boiling-point having the density 0·07. The solid hydrogen melts when the pressure of the saturated vapour reaches about 55 m.m. In order to determine the temperature two constant volume hydrogen thermometers were used. One at 0° C. contained hydrogen under a pressure of 269·8 m.m., and the other under a pressure of 127 m.m. The mean temperature of the solid was found to be 16° absolute under a pressure of 35 m.m. All the attempts made to get an accurate electric resistance thermometer for such low temperature observations have been so far unsatisfactory. Now that pure helium is definitely proved to be more volatile than hydrogen, this body, after passing through a spiral glass tube immersed in liquid hydrogen to separate all other gases, must be compared with the hydrogen thermometer. For the present the boiling-point which is 21° absolute at 760 m.m., compared with the boiling-point at 35 m.m. or 16° absolute, enables the following approximate formula for the vapour tension of liquid hydrogen below one atmosphere pressure to be derived:—

$$\log p - 6{\cdot}7341 - 83{\cdot}28/T \text{ m.m.},$$

where T = absolute temperature, and the pressure is in m.m. This formula gives us for 55 m.m. a temperature of 16·7° absolute. The melting-point of hydrogen must therefore be about 16° or 17° absolute. It has to be noted that the pressure in the constant volume hydrogen thermometer, used to determine the temperature of solid hydrogen boiling under 35 m.m., had been so far reduced that the measurements were made under from one-half to one-fourth the saturation pressure for the temperature. When the same thermometers were used to determine the boiling-point of hydrogen at atmospheric pressure, the internal gas pressure was only reduced to one-thirteenth the saturation pressure for the temperatures. The absolute accuracy of the boiling-points under diminished pressure must be examined in some future paper. The practical limit of temperature we can command by the evaporation of solid hydrogen is from 14° to 15° absolute. In passing it may be noted that the critical temperature of hydrogen being 30° to 32° absolute, the melting-point is about half the critical temperature. The melting-point of nitrogen is also about half its critical temperature. The foam-like appearance of the solid when produced in an ordinary vacuum is due to the small density of the liquid, and the fact that rapid ebullition is substantially taking place in the whole mass of liquid. The last doubt as to the possibility of solid hydrogen having a metallic character has been removed, and for the future hydrogen must be classed among the non-metallic elements.

Estimation of Mannose mixed with other Sugars.—Em. Bourquelot and H. Hérissey.—During researches on the composition of certain albumens, the authors were led to investigate in what measure the property possessed by mannose of giving a hydrazone insoluble in the cold could be used for an estimation of this sugar. To do this, a series of experiments were made on solutions containing known quantities of mannose mixed with other sugars. The quantity of mannose hydrazine precipitated was determined and compared with the original quantity of mannose. It was found that phenylhydrazine can be used to estimate mannose in researches in vegetable chemistry, and that the presence of other sugars does not sensibly modify the results. As low a temperature as possible should be used, and only solutions containing from 3 to 6 per cent of mannose.—*Comptes Rendus*, cxxix., No. 6.

ON CHROMYLAMIDE, $CrO_2<^{NH_2}_{NH_2}$.

By JULIUS OHLY, Ph.D.

IF bichromate of potassium is warmed with hydrochloric acid, the salt is transposed according to Equation 1 :—

1. $K_2Cr_2O_7+2HCl=2CrO_2<^{Cl}_{OK}+H_2O$

into potassium chlorochromate and water. Heintze succeeded in producing a substitution-product of the formula $CrO_2<^{NH_2}_{OK}$, and of dark ruby colour, by treating the chlorochromate obtained in 1 with dry ammonia gas, as shown in Equation 2,—

2. $CrO_2<^{Cl}_{OK}+NH_3=CrO_2<^{NH_2}_{OK}+HCl.$

He has described his method of preparing the salt, and by following his directions closely I also obtained it. If the product resulting under these conditions is dissolved in distilled water, a concentrated solution of ammonia (aqueous) added, and the mixture covered with a layer of ether, and dry chlorine gas conducted into it at common temperature, a lively reaction sets in, in the course of which the solution assumes a light brown colour and becomes clear (Equation 3) :—

3. $CrO_2<^{NH_2}_{OK}+2NH_4OH+Cl_2=$

$$=CrO_2<^{NH_2}_{NH_2}+KClO+NH_4Cl+2H_2O.$$

On letting this solution stand for forty-eight hours, yellowish brown, dull, metallic leaflets crystallised out.

They proved to be the expected chromylamide, which was found to be soluble in water, and to produce ammonia in plenty when rubbed together with soda-lime in a mortar. The solution of the amide in water was tested with silver nitrate and lead acetate, and gave the characteristic reactions of the amides.

Repeated analyses, the one made by decomposing a weighed quantity of the amide by means of hydrochloric acid and subsequent precipitation, the other by decomposing the compound through heat, which is very readily accomplished, showed it to be chromylamide, corresponding to the formula $CrO_2<^{NH_2}_{NH_2}$.

I have also tried to obtain the corresponding manganese compound, so far, however, with but indifferent success.

ACTION OF NITRATE OF SILVER ON THE FATTY ACIDS OF COTTON-SEED OIL.

By EUG. CHARABOT and M. MARCH.

M. MILLIAU has proposed a method for the detection of cotton-seed oil in olive oil, which is a great improvement on that of M. Becchi. This latter consisted, as will be remembered, of roughly treating the suspected oil with nitrate of silver. M. Milliau submits, not the oil itself, but its products of saponification to the action of the same reagent. Neither of the above-mentioned chemists, however, have attempted to establish the nature of the brown precipitate obtained by this treatment.

In 1895, M. Dupont (*Bull. Soc. Chim.*, Series 3, vol. xiii., pp. 696 and 775), in the course of a research on cotton-seed oil and its detection in American lards, discovered in this oil a volatile sulphurised substance.

Shortly afterwards, M. Dupont and one of us (Dupont and Charabot, *Bull. Soc. Chim.*, series 3, vol. xv., p. 341) met with an analogous volatile sulphide in authentic olive oil. They concluded that the black precipitate obtained with nitrate of silver might contain sulphide of silver, and that consequently the formation of a similar precipitate would not be an invariable proof of fraud. No experiment, however, was made with a view to determining its chemical composition. We have therefore undertaken to decide this question.

Before commencing the study of the brown substance, which occurs when the fatty acids of cotton-seed oil are treated with nitrate of silver, it was interesting to find out whether, in the course of the preparation of these fatty acids, the sulphurised substance discovered by M. Dupont would be eliminated or not.

For preparing the fatty acids we followed the method described by MM. Müntz, Durand, and Milliau, in their masterly report to the Minister of Agriculture (*Bull. du Ministère de l'Agriculture*, 1895, p. 143). The product obtained was washed a great number of times with distilled water until the *complete elimination* of the sulphuric acid.

About 5 grms. of the thus purified fatty acid were oxidised by heating for six hours with a pure concentrated solution of permanganate of potash on a water-bath; the oxide of manganese was then dissolved in pure warm hydrochloric acid; the fatty acids were separated by filtration, and the clear liquid concentrated by evaporation.

The addition of nitrate of barium caused the formation of a precipitate of sulphate of barium insoluble in acids; thus the sulphurised matter in the cotton-seed oil was not eliminated during the preparation of the fatty acids.

We repeated the operation without using sulphuric acid, but using hydrochloric acid, which had already been tested and found perfectly pure. The results obtained were just as conclusive.

About 50 grms. of cotton-seed oil were then saponified, the fatty acids set at liberty, purified and treated with 3 per cent nitrate of silver on the water-bath; this placed us under exactly the conditions described by M. Milliau. A brown precipitate is formed, which we allowed to cool away from the light; this was collected on a filter, and washed a number of times with warm water.

The fatty acids were removed from the precipitate remaining on the filter by washing with alcohol at 90°; the insoluble product was then exhausted successively with ligroïn, benzene free from thiophene, and ether. There finally remained a dark brown, homogeneous dry substance. This substance was powdered, and then treated with warm, dilute hydrochloric acid; very gradually a precipitate of chloride of silver was formed, and at the same time a fatty acid set at liberty.

This fatty acid, after being purified by solution in benzene and filtration of the solution, melts at 52° and solidifies at 49—50°. It gives a white ammoniacal salt, which, treated with nitrate of silver, gives a brown precipitate analogous to that from which it started.

Another portion of the brown precipitate, obtained by the action of nitrate of silver on the fatty acids of cotton-seed oil, was oxidised by heating for two hours with a pure concentrated solution of permanganate of potash on the water-bath. The oxide of manganese was dissolved by the addition of hydrochloric acid. Small oily drops collect on the surface of the liquid, and a precipitate of chloride of silver is formed; the solution is filtered and concentrated by evaporation. On adding nitrate of barium a precipitate of sulphate of barium is formed; this precipitate is very apparent, even when operating on only 1 grm. of the brown substance.

To sum up—1. The fatty acids obtained by the saponification of cotton-seed oil and precipitation by means of mineral acids are not free from sulphurised material. 2. The brown precipitate formed, when we treat these acids with nitrate of silver, contains principally the silver salt of an acid fusible at 52° and sulphide of silver.

Olive oil, which contains a sulphurised substance analogous to that of cotton-seed oil, would therefore be susceptible of giving with nitrate of silver a more or less distinct black precipitate of sulphide of silver. It is, therefore, unnecessary to insist too much on the care with which opinions should be formed when we have to deal with the search for cotton-seed oil in olive oil.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 11.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E., *Water Examiner, Metropolis Water Act*, 1871.

London, August 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

We have to record a continuation of the drought. Rain has fallen at Oxford on nine days only, the total amount being 1·32 inches, of which 0·76 inch, or more than half, fell on the 22nd. As the average amount for thirty years is 2·68 inches, we have a deficiency of 1·36 inches. This makes a total deficiency for the year of 3·11 inches, or 22·7 per cent.

Our bacteriological examinations of 383 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, standpipes, &c., making a total of 422 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	1858
New River, filtered (mean of 77 samples) ..	30
Thames, unfiltered (mean of 26 samples) ..	1270
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 203 samples)	41
Ditto ditto .. .. highest	430
Ditto ditto .. .. lowest	1
River Lea, unfiltered (mean of 26 samples) ..	4357
River Lea, from the East London Company's clear water well (mean of 25 samples) . ..	26

It has always seemed to us to be both unfair and misleading to test the bacterial quality of a water from an examination of a sample drawn from a standpipe or fire plug. The only correct, and by far the most direct test of efficient microbic purification by any filtration process, is to secure samples of the water immediately after filtration and before it passes into the distributing mains.

However good water may be at its source, it will always deteriorate more or less in the mains. This will occur with any supply, whether it be derived from the Thames, from Wales, or from chalk wells. There is no known mode of avoiding bacterial increase after the water passes into the mains and pipes of a great city like London; that is to say, the number of microbes always largely increases during its wide distribution and circulation through the labyrinth of pipes; but the additional microbes so generated are known by experience and observation to be harmless.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 7, August 14, 1899.

Researches on Metallic Derivatives of Acetylene.—MM. Berthelot and Delépine.—The authors have experimented on the compounds of acetylene with silver, silver nitrate, sulphate, chloride, and iodide. When heated in a vacuum, dry silver acetylide, Ag_2C_2, detonates, with formation of a reddish flame. This flame is scarcely to be expected, since the products of the explosion are solids, silver and carbon. However, investigation of this matter leads to the conclusion that the temperature of the reaction is high enough to volatilise the carbon, and that the flame is gaseous carbon at a very high temperature, probably approaching 4000° C.

Reaction of Argon and Nitrogen with Mercury Alkyls. — M. Berthelot. — When mercury methyl, $Hg(CH_3)_2$, is placed in an atmosphere of argon and subjected to the silent electric discharge no compound with argon is formed, but when the argon is replaced by nitrogen a rapid absorption of the latter takes place.

Action of Sodammonium and Potassammonium on Tellurium and Sulphur.—C. Hugot.—In the presence of excess of the alkali two amorphous tellurides are formed, Na_2Te and K_2Te, both being white and insoluble in liquid ammonia gas. By making use of this latter property, the tellurides are separated from excess of ammonium alkali. By merely substituting sulphur for tellurium, the two monosulphides Na_2S and K_2S are formed. When tellurium is used in large excess, the tellurides Na_2Te_3 and K_2Te_3 are formed, which resemble the former in appearance. In the case of excess of sulphur being used, Na_2S_5 and Na_2Te_3 are formed, which absorb ammonia gas.

Estimation of Free Phosphorus in Oils and Fatty Bodies.—E. Louïse.—The author proposes the following method for the estimation of free phosphorus in fatty substances, since it is available even when the phosphorus exists in mere traces:—A concentrated solution of silver nitrate is added to the oil in the presence of about twenty times its volume of acetone. The black precipitate obtained is, all other things being equal, proportional to the quantity of free phosphorus present in the oil. Acetone possesses the property of dissolving both oil and water at the same time, hence the drops of aqueous solution necessary to precipitate the phosphorus do not separate out.

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DAVID LEWIS, Treasurer.

Treasurer's Chambers, 20, York Place,
Edinburgh, August 1, 1899.

THE CHEMICAL NEWS.

Vol. LXXX., No. 2078.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Dover, 1899.

By HORACE T. BROWN, LL.D., F.R.S.,
President of the Section.

The subject which I have chosen for my Address is the fixation of carbon by plants, one which is the common meeting ground of Chemistry, Physics, and Biology. I must, however, confine myself only to certain aspects of the question, since it is manifestly impossible to fully discuss the whole of a subject of such magnitude and importance within the time at my disposal.

We have become so acustomed to the idea that the higher plants derive *the whole* of their carbon from atmospheric sources, that we are apt to forget how very indirect is the nature of much of the experimental evidence on which this belief is founded. There can, of course, be no doubt that the primary source of the organic carbon of the soil, and of the plants growing on it, is the atmosphere; but of late years there has been such an accumulation of evidence tending to show that the higher plants are capable of being nourished by the direct application of a great variety of ready-formed organic compounds, that we are justified in demanding further proof that the stores of organic substances in the soil must necessarily be oxidised down to the lowest possible point before their carbon is once more in a fit state to be assimilated.

It was the hope of gaining more direct evidence on this important question which led me some time ago to attack the problem experimentally in conjunction with Mr. F. Escombe, the resources of the Jodrell Laboratory at Kew having been kindly put at our disposal by Sir W. Thiselton Dyer and Dr. D. H. Scott. Up to the present time our experiments have not been carried far enough to enable us to give a positive answer to the main question, but they have already suggested a new method of attack which will enable us in the future to determine, with a fair amount of certainty, whether any particular plant, growing under perfectly natural conditions, derives any appreciable portion of its carbon from any other source than the gaseous carbon dioxide of the atmosphere.

During the course of the inquiry many interesting side issues have been raised which we believe to be of some importance in their bearing on the processes of plant nutrition, and it is to a consideration of these that I intend to devote the greater part of my Address.

I must, however, in the first place indulge in a little historical retrospect, and am the more tempted to do this, as far as the early pioneers in this branch of knowledge are concerned, since a critical study of their writings has shown me very clearly that the relative merits of some of these older workers, and the respective parts which they took in founding the true theory of assimilation, have in our own time been much misrepresented by more than one historian of science whose name carries great weight.

There is no chapter in the history of scientific discovery of greater abiding interest than that which was opened by Priestley in 1771, when he commenced his work on the influence of plants on the composition of the air around them. It has often been assumed that these experiments of Priestley, which were unquestionably the starting-point for all succeeding workers, were the result of some haphazard method of working, and of one of those happy chances to which he is in the habit of attributing some of his most important discoveries. However much the element of chance entered into some of his work—and in this respect I think Priestley often does himself injustice—the discovery of the amelioration of vitiated air by plants was certainly not a case of this kind. Of all his contemporaries belonging to the old school of Chemistry Priestley had the clearest conception of the processes of animal respiration and of their identity with the process of combustion. This is clearly shown by his "Observations on Respiration and the Use of the Blood," which he presented to the Royal Society in 1776. This memoir, written of course from the phlogistic point of view, only requires translating into the language of the newer Chemistry to be an accurate statement of the main facts of animal respiration. We have it on Priestley's own authority that it was these studies which produced in his mind a conviction that there must be some provision in Nature for dephlogisticating the air which was constantly being vitiated by the processes of respiration, combustion, and putrefaction, and for rendering it once more fit for maintaining animal life. In his search for this compensating influence, which he justly regarded as one of the most important problems of natural philosophy, he made many attempts to bring back the vitiated air to its original state by agitating it with water, and by submitting it to the continued action of light and heat, and it was in the course of these systematic attempts that he was led to study the influence of plants in this direction.

It was in the month of August, 1771, that he made the memorable experiments at Leeds of immersing sprigs of mint in air which had been vitiated by the burning of a candle or by animal respiration. To quote his own words, this observation led him "to conclude that plants, instead of affecting the air in the same manner with animal respiration, reverse the effects of breathing, and tend to keep the atmosphere sweet and wholesome when it is become noxious in consequence of animals either living or breathing, or dying and putrefying in it." That he was fully convinced that these observations, which he repeated and amplified in the following year, presented the true key to the problem, is sufficiently shown by another passage in which he says:—"These proofs of the partial restoration of air by plants in a state of vegetation, though in a confined and unnatural situation, cannot but render it highly probable that the injury which is continually done to the atmosphere by the respiration of such a number of animals, and the putrefaction of such masses of both vegetable and animal matter, is, in part at least, repaired by the vegetable creation; and notwithstanding the prodigious mass of air that is corrupted daily by the above causes, yet if we consider the immense profusion of vegetables upon the face of the earth growing in places suited to their nature, and consequently at full liberty to exert all their powers, both inhaling and exhaling, it can hardly be thought but that it may be a sufficient counterbalance to it, and that the remedy is adequate to the evil."

Between the time of Priestley temporarily relinquishing his experiments in this direction in 1772, and his resumption of them in 1778, owing to the adverse criticism of Scheele and others, he had discovered dephlogisticated air or oxygen, and had elaborated his method for ascertaining the purity of air, or its richness in oxygen, by determining its diminution in volume after mixing with an excess of nitric oxide over water.* This method gave of course a much greater degree of precision to his results than was attainable in his earlier work, where the purity of the air at the end of an experiment was only determined by ascertaining if it would support the combustion of a candle or allow a small animal to live in it.

The results of his later work were published in 1799, and were not altogether confirmatory of those arrived at six years before. It is true that he generally found

* Nitric oxide was discovered by Priestley in 1772, and was described by him under the name of "nitrous air."

evidence of an evolution of oxygen by the plants, but occasionally the air was less "pure" at the end of an experiment than it was at the beginning, and this occurred in a sufficient number of cases to lead Priestley to doubt to some extent the accuracy of his previous conclusions. On the whole, however, he still thinks it *probable* that the vegetation of healthy plants has a salutary effect on the air in which they grow.

The reason for this want of complete consistency in these later experiments was, of course, his failure at that time to recognise the important influence of *light* in bringing about the evolution of oxygen, an explanation which was given shortly afterwards by Ingen-Housz.

Priestley's attention was now taken up with another observation, which led him within a very short distance indeed of the discovery that the evolution of oxygen by plants is conditioned not only by a sufficient degree of illumination, but also by the pre-existence of carbon dioxide. It is the more necessary to treat of this point somewhat in detail, since it is a part of his work which has received but scanty justice at the hands of recent writers, who have apparently failed to see how much our modern conceptions of plant nutrition really owe to the initiative of Priestley. In his "History of Botany," Sachs deals very unfairly with Priestley in this respect, owing to a want of intimate knowledge of his writings, and to the lack of anything like perspective in estimating the relative merits of his contemporaries Ingen-Housz and Senebier, whose position can only be completely understood after a careful study of their numerous original memoirs, some of which are by no means readily accessible.

In the course of his experiments on plants partially immersed in water more or less fully impregnated with "fixed air," Priestley had observed a fact which had not escaped the notice of Bonnet at an earlier date, that bubbles of gas arose spontaneously from the leaves and stems, and it occurred to him that an examination of the nature of this gas by means of his new eudiometric process ought to settle the question whether plants really do contribute in any way to the purification of ordinary air. It was in June, 1778, that he put this to the test, and he found that the air thus liberated was much richer in oxygen than ordinary air. On removing the plants he found to his astonishment that the water in which they had been placed, and which had a considerable amount of "green matter" adhering to the sides of the phials, still continued to evolve a gas which increased in amount when the vessels were placed in sunlight. On testing this gas with his eudiometric process, he found that it consisted to a great extent of "dephlogisticated air" or oxygen; in fact, from the experimental results which he gives, it is evident that the gas contained from 74 to 85 per cent of oxygen. Having observed that the "green matter" appeared much more readily in pump water than in rain or river water, and knowing that pump water contained considerable amounts of "fixed air," he was led to make a series of experiments with water artificially impregnated with carbon dioxide, which left no doubt in his mind that the production of the "green matter" and the evolution of dephlogisticated air were in some way due to the presence of "fixed air." Up to this point Priestley was following a path which seemed about to lead him to a complete solution of his previous difficulties. He had beyond all question succeeded in showing that the evolution of oxygen was not only dependent on the pre-existence of carbon dioxide, but that light was also required for the process. It only wanted, in fact, the recognition of the vegetable nature of the alga which constituted his "green substance" to bring these observations into line with his previous work, and to complete a discovery which would have eclipsed in importance all the others with which Priestley's name is associated. It was just this one step which he most provokingly failed to take. It is true that he examined the "green substance" under the microscope, but owing to want of skill in the use of the instrument, and also to his defective eyesight, he was unable to determine its true nature, and unfortunately adopted the view that it had merely a mechanical action in separating the oxygen from the water, and, to use his own words, that "it was only a circumstance preceding the spontaneous emission of the air from water." He was in fact now inclined to regard the process as a purely chemical one, due to the direct action of light on the carbon dioxide dissolved in the water.

But this was by no means Priestley's final view, as shown by a further description of his experiments on plants set forth in the new edition of his works published in 1790, where he clearly recognised the error into which he had been led.* Meanwhile the subject had been taken up by two other observers, Ingen-Housz and Senebier, and in order to thoroughly understand the respective shares which these men took in advancing our knowledge of the assimilatory process, it is necessary to consult not only their books, but also the numerous scattered memoirs which appeared at intervals between the years 1779 and 1800.

To Ingen-Housz must unquestionably be awarded the merit of having experimentally demonstrated that the amelioration of the surrounding air by plants is not—as Priestley at first believed—due to vegetative action *per se*, but is dependent on the access of light of a sufficient degree of intensity, and, moreover, that the power is confined to the green parts of the plants. At the same time, whilst recognising, as Priestley had done before him, that the combined action of plants and light on the air was a dephlogisticating process, he did not know, until after its demonstration by Senebier, that the particular form of phlogisticated air which was essential to plants was "fixed air" or carbon dioxide. In fact Ingen-Housz had but a slender knowledge of the chemistry of his day; so much so indeed that he constantly confuses "phlogisticated air" or nitrogen with "fixed air," and attributes the source of the evolved oxygen either to air imprisoned within the leaf, or, in the case of submerged plants, to a metamorphosis of the water itself. I must, however, recall the fact that Ingen-Housz was the first to show that the green parts of plants in the dark, and the roots both in the light and in darkness, vitiate the air in the same way as animals do. Oh the strength of these experiments he is generally given credit for having first observed the true respiration of plants; but I cannot avoid the conclusion that, in the controversy which ensued on this point between Ingen-Housz and Senebier, the adverse criticisms of the latter were well founded. Whilst not denying that plants in the dark have some mephitic influence on the air around them, Senebier maintained that the greater part of the observed effect was due to a fermentative action set up in the large bulk of leaves which Ingen-Housz employed. Certainly some of the results appear to be largely in excess of those we should now expect to obtain from respiratory processes only.†

Senebier's work falls between the years 1782 and 1800. The fact that he was an early convert to the new ideas

* The view which was taken by Priestley's contemporaries of his position with regard to the discovery of the fundamental facts is well exemplified by the following remarks taken from a paper published by Ingen-Housz in 1784 (*Annales de Physiques*, xxiv., 44):—"C'est à M. Priestley seul que nous devons la grande découverte que les végétaux possèdent le pouvoir de corriger l'air mauvais, et d'améliorer l'air commun; c'est lui qui nous en a ouvert la porte. J'ai été assez constamment attaché á ce beau système, dans le temps que lui même, par trop peu de prédilection pour ses propres opinions, paroissoit chanceler."

† It is by no means uncommon to find Ingen-Housz put forward as the discoverer of the fixation of carbon by plants from carbon dioxide. This claim is generally based on certain statements made in his essay on the "Food of Plants and the Renovation of the Soil," published in 1796 as an Appendix to the outlines of the fifteenth chapter of the "Proposed General Report from the Board of Agriculture." All that is good and sound in this essay is taken from Senebier's papers without any acknowledgment, but, in appropriating ideas which he evidently understands very imperfectly, he has built up a system of plant economy which is almost unintelligible.

and generalisations of Lavoisier gives his views on plant nutrition far greater precision than those of Priestley and Ingen-Housz. His experiments, for the most part well-devised, proved beyond all doubt that the oxygen disengaged from submerged and insolated plants could not be derived from air contained in the leaf parenchyma, but that it depended on the pre-existence of carbon dioxide, and that its evolution was strictly proportional to the amount of carbon dioxide which the water contained.

Although positive experimental proof was still wanting that aërial plants also derive their carbon from carbon dioxide, Senebier regarded this as extremely probable; but, taking into consideration the small amount of this gas present in the atmosphere, he concluded that it must reach the plant by the roots and leaves entirely in a state of solution in water.

The work of Priestley, Senebier, and Ingen-Housz fortunately attracted the attention of a young chemist of high attainments, who, within a period of less than ten years, did more for the advancement of vegetable physiology than any single observer before or since his time. Théodore de Saussure, the second of that illustrious name, and the son of the famous explorer and natural philosopher, commenced his researches about the year 1796, and in 1804 published his "Recherches Chimiques sur la Végétation," a modest little octavo volume of some 300 pages, which must certainly take rank as one of the great classics of scientific literature, and one of the most remarkable books of the century.

De Saussure was a past master in the art of experiment, and the methods which he devised for demonstrating the influence of water, air, and soil on vegetation have been the models on which all such investigations have been conducted ever since. It is indeed very difficult, when reading this masterly essay, to bear in mind that it was not written fifty or sixty years later than the date on its title-page, so essentially modern are its modes of expression and reasoning, and so far is the author in advance of his contemporaries. It is to this work we must refer for the first experimental proof that plants derive at any rate the greater part of their carbon from the surrounding atmosphere. This was shown by De Saussure by a variety of quantitative experiments of a sufficient degree of accuracy to bring out the great leading facts. By making known mixtures of carbon dioxide and air, and submitting them to the action of plants in sunlight, he was able not only to show that the gaseous carbon dioxide was decomposed and the carbon assimilated, but also that the volume of oxygen disengaged was approximately equal to that of the carbon dioxide decomposed.* He also showed that plants growing in the open in moist sand, or in distilled water, and therefore under conditions in which they could not derive any carbon from other than atmospheric sources, not only materially increased in dry weight, but contained much more carbon at the close of the experiment than at the beginning, and had also fixed an appreciable amount of water in the process. That atmospheric carbon dioxide is not only beneficial to plants in sunlight, but is also essential to their very existence, De Saussure proved by introducing an absorbent of this gas into the vessel containing a plant or the branch of a tree rooted naturally in the soil. Under these conditions the portions of the plant enclosed always died. He also ascertained by experiment the increase in dry weight of a sunflower plant during four months of natural growth; and knowing approximately the amount of water transpired during that period, and the maximum amount of solids which this transpired water could possibly introduce into the plant, he calculated that these solids, and the carbon dioxide in solution in the transpiration water, fell far short of accounting for the observed increase in the dry weight of the plant. This increase must, therefore, be mainly due to the fixation of atmospheric carbon dioxide and water.

It is certainly a remarkable fact that the rigid experimental proofs which De Saussure brought forward in support of his views did not carry conviction to the minds of everyone. His book, however, suffered the fate of many others which have appeared in advance of their time. It is true that De Saussure's doctrines were always kept alive by the advanced physiologists of the French school, such as DeCandolle and Dutrochet; but when Liebig first turned his attention to the subject he found the field in possession of the humus theory of Treviranus, a theory which no longer took any account of the decomposition of carbon dioxide by the leaves, but which derived the whole of the elements of the growing plant from a solution of the soil extract taken up by the roots. We may well say with Sachs, "Nothing can be conceived more deplorable than this theory of nutrition; it would have been bad at the end of the seventeenth century, it is difficult to believe that it could have been published thirty years after De Saussure's work." It is well known how, by the cogency of his reasoning and the force of his genius, Liebig successfully overthrew this heresy, and once more established the doctrine of carbon assimilation as taught by De Saussure; and the accurate work of Boussingault, who, whilst elaborating far more delicate analytical processes than were possessed by chemists in the early days of the century, still in the main used De Saussure's methods, gave the final death-blow to the humus theory, at any rate in the crude form in which it was presented by its originators. No one since that time has questioned the fact that green plants owe the greater part of their carbon to atmospheric sources, and the accumulated experience of two succeeding generations of workers has added proof on proof of the correctness of this great generalisation.

But whilst it cannot be doubted that green plants devoid of parasitic or saprophytic habit derive the principal part of their carbon from the air, is the experimental evidence at present so complete as to exclude all other sources of supply? De Saussure himself certainly left the door open to such a possibility, and although Boussingault held a different view, we find Sachs as late as 1865 maintaining that it is not contrary to the generally accepted theory of assimilation to suppose that there are chlorophyllous plants which decompose carbon dioxide and at the same time absorb ready-formed organic substances whose carbon they utilise in the formation of new organs.

Up to comparatively recently there was little or no experimental evidence to justify this supposition, for the early experiments of De Saussure on the influence of solutions of sugar, and of other organic substances, on growing plants, although very suggestive, were not of a sufficiently precise nature to lead to any conclusions, and we must come down to within fifteen years of the present time for anything like a demonstration that the green organs of plants can, under favourable conditions, build up their tissue from already elaborated carbon compounds just as do the fungi and the non-chlorophyllous plants generally.

The active centres of the decomposition of carbon dioxide in green leaves are the chlorophyll corpuscles or chloroplastids, and the first visible indication of this decomposition is the formation within these chloroplastids of minute granules of starch whose presence can be shown by suitable micro-chemical means. I have elsewhere discussed the question of how far the appearance of this starch is dependent on the pre-existence of other carbohydrates of a simpler constitution, and also the probability that the whole of the products of assimilation do not necessarily pass through the form of starch: this is a subject which need scarcely concern us at the present moment: it is sufficient to draw attention to the main fact that in an assimilating cell the chloroplastids, in the

* Although clearly indicating that no change of volume occurred in the mixture of air and carbon dioxide so treated, his final analytical results show a small apparent evolution of nitrogen. This was due to the eudiometric methods he employed,—methods, it is true, far superior in point of accuracy to those of his predecessors, but still necessarily imperfect.

vast majority of cases, give rise to these minute starch granules, which once more disappear when the plant is placed in darkness, or when the air around it is deprived of carbon dioxide. Now in 1883 Böhm made the interesting discovery that when green leaves are placed in the dark until the starch of their chloroplastids has completely disappeared, there is a reappearance of starch when the cut end of the leaf-stalk is immersed in a solution of cane-sugar and of dextrose, or when the leaf is brought directly in contact with solutions of these substances. He found, in fact, that the elements of the cell which, under ordinary circumstances, manufacture their materials for plant growth by the reduction of carbon dioxide under the influence of sunlight, can, under other conditions, supply their requirements from suitable ready-formed organic substances. These observations of Böhm were fully confirmed two years later by Schimper, and were subsequently much extended by A. Meyer and E. Laurent, who found that fructose, maltose, mannitol, dulcitol, and glycerol could also contribute directly to the nutrition of leaves.

Bokorny, working with *Spirogyra* immersed in dilute solutions, found that starch production in the chlorophyll bodies could be induced by a large number of organic substances, including, amongst many others, asparagin, citric, tartaric, and lactic acids, leucine, tyrosine, and peptone.*

Very much more to the point are the experiments of Acton, made in 1889, and the still more recent work of J. Laurent and of Mazé.

In his experiments on terrestrial plants Acton, after depleting them of starch, immersed the cut branches or roots, as the case might be, in culture fluids containing certain organic substances, and took precautions to prevent any normal assimilation from taking place by depriving the air around the plant of any trace of carbon dioxide. He was not able to show the direct nutritive influence of so large a range of substances as Bokorny had done for *Spirogyra*, but his results leave no room for doubt that several of the carbohydrates, and even glycerin, can be absorbed by the roots, and can contribute to the nutrition of the green parts. Acton tried, amongst other substances, an "extract of natural humus," which was an aqueous solution of the extractives of a light soil which are soluble in dilute alcohol. This extract was found to be effective in producing a small quantity of starch in the leaves, and it evidently contained some substance or substances directly assimilable by the plant.

Apparently without knowing anything of this work of Acton, J. Laurent has recently made a series of experiments on the culture of the maize plant in mineral solutions containing saccharose, glucose, or invert sugar, and in this way has not only obtained, as Acton had done before him, evidence of the active formation of starch in the leaves, but has also found a very notable increase in the dry weight of the plant. Although assimilation of the carbohydrate may under these circumstances go on in darkness, Laurent found that the process was much enhanced when light had access to the plant. Mazé, within the last few months, has obtained even more pronounced effects of this kind.

When all these new facts are taken into consideration, I think they justify what I have already said, that we ought to demand more direct evidence than is at present available before we accept the view that the majority of chlorophyllous plants take in *the whole* of their carbon from the atmosphere. In the cycle of change which the organic matter of the soil is constantly undergoing under the influence of micro-organisms, it seems by no means improbable that intermediate substances may be formed which in some measure directly contribute to the nutrition of the higher plants, and we must also by no means lose sight of the possible effect, in the same direction, of the symbiotic union of certain fungi with the root extremities of many plants, the Mycorhizæ, whose functions are still so imperfectly understood. Then, again, we must remember that we have another possible extra-atmospheric source of carbon dioxide in the transpiration water of the plant, which is derived from a soil whose gases may contain 5 per cent or more of carbon dioxide. From the amount of water transpired in a given time, and an application of the law of partial pressures, it may be readily shown that the supply of carbon dioxide to the aërial organs of a plant from this source is by no means negligible.

Before these problems can be attacked for a particular plant with any hope of success it is clear that we must have some means of establishing an accurate debtor and creditor account as between the plant and the surrounding atmosphere, and this account must extend over a sufficiently long period, and allow of an accurate balance being struck with the amount of carbon found in the plant at the end of the experiment.

Up to within a few years ago we had no means of even approximately determining the actual rate at which the assimilatory process goes on in a plant other than that afforded by its increase in weight in a given time. Such experiments, necessarily extending over weeks or months, can, at the best, only give us certain average results, and consequently afford no measure of the activity of assimilation under fixed conditions of insolation. In the year 1814 Sachs, who had for some time been at work on the formation of starch in leaves under the action of sunlight, found that the accumulation of freshly assimilated material in a leaf may, under favourable conditions, go on so rapidly as to give rise to a very appreciable increase of weight in the leaf lamina within the short space of a few hours. By observing at different times of the day the varying dry weight of equal areas of large leaves, Sachs obtained an approximate measure of the rate of the assimilatory process which he could express in terms of actual number of grms. of substance assimilated by a unit area of leaf in unit of time. In this manner he was able to show, for instance, that a sunflower leaf, whilst still attached to the plant, increases in weight when exposed to bright sunshine at the hourly rate of about 1 grm. per square metre of leaf area. In the case of similar leaves detached from the plant, and of course under conditions in which the products of assimilation were entirely accumulated in the leaf, he found an increase in weight of rather more than 1½ grm. per square metre per hour.

I was able to confirm this work of Sachs in the course of an investigation on the Chemistry of Leaves which I made with Dr. G. H. Morris in 1892-93, and there can be no doubt that the variations in the weight of leaves can be used as a fair index of the activity of a leaf in assimilating, but it is not a method which admits of much refinement of accuracy, owing, amongst other things, to the want of perfect symmetry in the leaves as regards thickness and density of the laminæ and to the possible migration of the assimilated material into the larger ribs, which of course cannot be included in the weighings.

It is evident that a far better plan of measuring the rate of assimilation under varying conditions would be the estimation of the actual amount of carbon dioxide entering a given area of the leaf in a certain time, and it was to the perfection of a method of this kind that Mr. Escombe and I first turned our attention.

In all previous attempts to measure the rate of ingress of carbon dioxide, such as those of Corenwinder, and

* By far the most interesting and important result of Bokorny is the proof he gives that formaldehyde is directly assimilable by *Spirogyra*. His early attempts to show this had been rendered abortive by the highly poisonous nature of this substance. The difficulty was surmounted by using a dilute solution of sodium oxymethylsulphonate, which on warming with water splits up into formaldehyde and acid sodium sulphite. To prevent the unfavourable action of the acid sodium sulphite, dipotassium or disodium phosphate was added to the plant cultures. In such a solution, with rigid exclusion of carbon dioxide, *Spirogyra majuscula* forms starch in its chlorophyll bodies, but the access of light appears to be necessary.

The importance of this experiment is very great in connection with Baeyer's well-known hypothesis that the first act of assimilation is the reduction of carbon dioxide and water to the state of formaldehyde.

more recently still of Mr. F. F. Blackman, it has been necessary to use air containing comparatively large quantities of carbon dioxide, amounting to 4 per cent and upwards. Interesting and useful as such experiments undoubtedly are from the point of view from which they were undertaken, we must not lose sight of the fact that such conditions are highly artificial, and very far removed from those under which a plant finds itself in the natural state, where its leaves are bathed with air containing not 4 or 5 per cent but only 0·03 per cent of carbon dioxide. I shall have occasion later on to show how remarkably the rate of intake of carbon dioxide into a plant is influenced by extremely small variations in the tension of that gas, and that on this account no deduction can be drawn as to the rate of assimilation under natural conditions from any experiments in which the air contains even so small an amount of carbon dioxide as 1 per cent.

Before proceeding further in this direction, however, it will be well to consider the amount of carbon dioxide which must enter a leaf in a given time in order to produce an influence on its weight comparable with that indicated by the Sachs method of weighing definite areas. For this purpose I will consider a leaf with which we have made many experiments—that of *Catalpa bignonioides*. It is a very symmetrical leaf and a good assimilator, and since the intake of carbon dioxide takes place only on the under side, the question to which I wish to draw your attention can be stated in a simple manner. When such a leaf is subjected to a modified form of the half-leaf weighing method of Sachs, into the details of which I cannot here enter, it may, under favourable conditions, show an increase in dry weight equal to about 1 grm. per square metre per hour. Since this increase in weight is due almost entirely to the formation of carbohydrates, we can calculate with a close approximation to accuracy the corresponding amount of carbon dioxide. This will of course depend, within certain narrow limits, on the nature of the carbohydrate formed. The formation of a grm. of starch requires 1·628 grms. of carbon dioxide, whilst an equal amount of a $C_6H_{12}O_6$ or a $C_{12}H_{22}O_{11}$ sugar require 1·466 and 1·543 grms. respectively. From the knowledge we possess of the nature of the carbohydrates of the leaf, we are quite sure that the mean of these values—that is, 1·545 grms.—must be very near the truth. This amount corresponds to 784 c.c. of carbon dioxide at normal temperature and pressure, which must represent the volume abstracted by the square metre of leaf surface in one hour from air containing only three parts of carbon dioxide in 10,000, supposing the method of leaf weighing to give correct results. We shall see later on that this intake can be verified by direct estimations; it is equivalent to the total amount of carbon dioxide in a column of air of a cross section equal to that of the leaf, and of a height of 26 decimetres.

The extraordinary power which an assimilating leaf possesses of abstracting carbon dioxide from the air is best shown by comparing it with an equal area of a freely exposed solution of caustic alkali. We have made a very large number of experiments on the rate at which atmospheric carbon dioxide can be taken up by a solution of caustic soda under varying conditions, and have been surprised to find how constant the absorption is. In a moderately still air a square metre of surface of such a freely exposed solution will absorb about 1200 c.c. of carbon dioxide per hour, and this can only be increased to about 1500 c.c. even if the dish is exposed to the full influence of a strong wind out in the open. When the surface of the liquid is constantly renewed during the experiment by means of a mechanical stirrer, the rate of absorption is not sensibly affected, providing the agitation does not appreciably increase the surface area, and considerable variations in the strength of the alkaline solution are also without any effect. On the other hand, slight variations in the tension of the carbon dioxide of the air have a marked influence on the rate of absorption, and in order to study this point we have constructed an apparatus which allows us to pass over an absorptive surface of liquid a current of air in a stratum of known thickness, and with a known average velocity.

By introducing definite amounts of carbon dioxide into this stream of air we have been able to determine the influence of its tension on the rate of absorption. At present we have only employed air containing amounts varying from 0·8 to 13 parts per 10,000; that is to say, from about one-quarter to a little more than four times the amount contained in normal air. Within these limits, and probably beyond them, the rate of absorption by the alkaline surface is strictly proportional to the tension of the carbon dioxide in the air current. I shall have occasion to show later on that the same rule holds good with regard to an assimilating leaf, and that in this case also, within certain limits, the intake of the gas is proportional to its tension.

The fact which I wish more particularly to bring out in these comparisons is that a leaf surface which is assimilating at the rate of 1 grm. of carbohydrate per square metre per hour is absorbing atmospheric carbon dioxide *more than half as fast as the same surface would do if wetted with a constantly renewed film of a strong solution of caustic alkali.*

From what I have just said about the influence of tension on the absorption of carbon dioxide by an assimilating leaf, it is clear that any attempts to determine by direct means the natural intake of that gas during assimilation must be made with *ordinary* air, and that such experiments can only be carried out on a comparatively large scale. We had in the first instance to devise an apparatus which would rapidly and completely absorb the whole of the carbon dioxide from a stream of air passing through it at the rate of from 100 to 200 litres per hour, and at the same time admit of an extremely accurate determination of the absorbed carbon dioxide.

The absorbing apparatus which we finally adopted is a modification of one used by Reiset in his estimations of the carbon dioxide of the atmosphere. It consists essentially of a glass tube 50 c.m. long, fixed vertically in a wide-mouthed glass vessel furnished with a second aperture and a tubulure. The height of the vertical tube is invariable, but its width is regulated according to the amount of air required to be drawn through the apparatus in a given time. The bottom of this tube is closed with a platinum or silver plate pierced with a large number of very small holes, and two other similar perforated plates are inserted in the tube at certain intervals. The upper part of the tube is put in connection with an aspirating water-pump, and the absorbing liquid is placed in the lower glass vessel, whose second tubulure is connected with the supply of air in which the carbon dioxide has to be determined. When the aspirator is started the liquid is first drawn up into the vertical tube, and the air then follows through the perforated plates which act as "scrubbers." Reiset, in his work, used baryta-water as the absorbent, an aliquot part of which was titrated before and after the experiment, the changes in the volume of the liquid being corrected for by certain devices which I need not describe.

The efficiency of the apparatus as a complete absorber of atmospheric carbon dioxide leaves nothing to be desired, but in dealing with large quantities of baryta solution, amounting to 400 c.c. or more, the errors due to inaccurate titrations, or to over or under estimation of the volume changes, are all thrown on the final result, of which they may form a considerable part. We have consequently altogether discarded the use of baryta as an absorbent in favour of caustic soda. The carbonate is estimated by a double titration process, suggested a few years ago by Hart, and we have succeeded in so far improving this method that there is no difficulty in determining in 100 c.c. of the alkaline solution an amount of carbonate corresponding to $\frac{1}{10}$ c.c. of carbon dioxide.

There is practically no limit to the amount of air which can be passed through an absorbing apparatus such as I have described, and one of very moderate dimensions will

allow from 100 to 150 litres per hour to pass with perfect safety. Larger amounts can be dealt with either by increasing the size of the apparatus or by using several smaller ones arranged in parallel.

With proper precautions, determinations can certainly be made to within 0·02 part of carbon dioxide in 10,000 of air, so that with an apparatus of this kind it is possible to estimate the intake of carbon dioxide into a leaf or plant from ordinary atmospheric air, and to keep a sufficiently rapid stream of air passing over the leaf to maintain the tension of the carbon dioxide only slightly below the normal amount.

The air is measured by carefully standardised meters, reading to about 20 c.c.; and since the amounts of air aspirated vary from 100 to 900 litres or more, there are practically no errors of measurement. The tension at which the air passes through the absorption apparatus is measured by a manometer, and all the volumes are reduced to standard temperature and pressure.

All such experiments of course necessitate not only a determination of the carbon dioxide in the air which has passed over the leaf or plant, but also a simultaneous determination of the carbon dioxide in the ordinary air used. The accumulation of these air determinations clearly shows that the ordinary statements of our text-books as to the amount of carbon dioxide and its limits of variation are altogether misleading.

In our experiments the air was in all cases taken from a height of 4 feet 6 inches from the ground, the amounts aspirated varying from 100 to 500 litres.

In the month of July, 1898, the minimum amount of carbon dioxide found was 2·71 parts per 10,000 of air, and the maximum 2·86. During the winter months, when the ground was almost bare of vegetation, it rose to from 3·00 to 3·23 parts per 10,000; and on one foggy day, March 16, 1899, after a whole week of similar weather, we found the very exceptional amount of 3·62. As a rule we may take it that the amount of carbon dioxide in the atmosphere during the period of greatest plant growth rarely falls short of 2·7 parts per 10,000, and rarely exceeds 3·0 parts, with an average of about 2·85. These numbers come very close to the determinations of Reiset, and of Müntz and Aubin, and agree also fairly well with the Montsouris determinations.

(To be continued).

PROPOSED INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.*

By Professor F. W. CLARKE.

(*Letter to Professor* W. A. TILDEN).

Washington, D.C., July 19, 1899.

DEAR SIR,—In response to your letter of June 8, I take pleasure in sending you a statement of my views relative to the proposed International Committee upon Atomic Weights. The suggestions which I have to offer are, however, only my own individual opinions, and are not to be regarded as representing any organisation, or as based upon any definite programme. Still, they may serve as a basis for discussion, and so help to clear a way for progress.

Every chemist who has studied, with any closeness, the determination of atomic weights, has noticed the discordance which exists among the published tables. In many text-books and works of reference tables are given which seem to have been edited with a pair of scissors and a paste-pot, and which show about as much critical acumen in their making up as those useful implements could furnish. Not only are obsolete values found persisting, but values are given which are inconsistent among themselves; and occasionally there is evidence of the most pitiable confusion as to the fundamental standards of reference. One table is based upon the standard of oxygen as 16; another upon oxygen as 15·88, and still others upon the wholly erroneous ratio of 15·96. In one and the same table these several standards may simultaneously appear, one atomic weight being referred to one, and another to another; the compiler being quite unconscious of the discrepancy. Tables of atomic weights which were good ten years ago reappear frequently in books of to-day, with no hint that any changes have occurred in any of the data.

In order to remedy, at least in part, this unnecessary confusion in our fundamental constants, the American Chemical Society in 1892 requested me to prepare an annual report upon atomic weights. Each year since I have submitted to the Society such a report (six in all), giving a summary of the determinations made, and a table of values brought down to the date of publication. So far as it went, the work seems to have been useful; but it did not go far enough, and it carried only the authority which might attach to the opinions of a single individual. More criticism, more comparison of views among chemists, was evidently desirable; and the movement in favour of international action seems to be a movement in the proper direction.

In 1898 the subject was taken up independently by the German Chemical Society, which appointed a committee consisting of Landolt, Ostwald, and Seubert. This committee in due time reported a table of atomic weights, recommending the adoption of O=16 as the standard of reference, and suggested that like committees might well be appointed by other societies for purposes of co-operation. Acting upon that suggestion, the American Chemical Society, at its last general meeting, appointed a committee consisting of F. W. Clarke, J. W. Mallet, E. W. Morley, T. W. Richards, and Edgar F. Smith; and that committee has already begun correspondence with the English and German organisations. A number of local societies in various parts of Europe have recommended the use of the table put forth by the German Committee; but a full conference of all the parties at interest is yet to be held. Probably an effort will be made to discuss the atomic weight question at the Congress of Chemists in Paris next year; but this proposition is so far only a matter under consideration. At all events, a general international committee might then be most readily brought together; and its recommendations would certainly carry much weight.

What, now, could such a committee accomplish? In what directions should its influence be exerted? These are questions to be answered beforehand, for upon the answers the expediency of definite action must depend. Unless we have a reasonable expectation that something useful can be done, it is not worth while to go any further.

Two lines of discussion for the proposed committee are self-evident:—First, a discussion of the ultimate standard of reference, whether it shall be O=16 or H=1, and upon this question there are legitimate differences of opinion; secondly, a discussion of the existing data, in order to determine the most probable values for the atomic weights, and to get some insight into their relative accuracy. This involves the preparation of a table of atomic weights for practical use, in which some indication shall be given as to the trustworthiness of the individual values. Which figures have been well determined, and which need correction, should be clearly shown, and in that way future investigation would be stimulated. Such a table would call for revision from time to time, perhaps annually, and for this reason the committee should be made a permanent body, to act either by meeting or by correspondence, according to circumstances. Only an international committee could expect to have its findings generally accepted.

Up to this point the work proposed for the committee has already been done, with more or less thoroughness,

* Read before the British Association (Section B), Dover Meeting, 1899.

by the German committee, by Professor Richards, and by myself; so that the ground is pretty well cleared, and the field of action can be seen. But still more is desirable; and just here, I believe, the task of the proposed committee may become most important. Having ascertained the weak points in our system of atomic weights, the next thing to do is to have them strengthened; and to this end the combined influence of a body of trained experts might well be exerted. At present, all research in this field of investigation is individual, and consequently the more obvious problems are simultaneously attacked by sometimes several independent workers, while other equally important questions are entirely neglected. A division of the field of labour, and co-operation in research, might easily be brought about; not by any exercise of authority on the part of the committee, but but by mutual consent of the investigators, working in conference, and aided by the suggestions which the international body might develop. In short, the committee could not order, but it might persuade; and in this direction its influence ought to be decidedly beneficial. Even if it did no more than to point out the essential problems to be solved, it would fully justify its existence.

There is one more general problem which the proposed committee should consider: that of methods. What are the best experimental methods for the determination of atomic weight ratios, and how shall the data be handled mathematically? On each division of this question there is something to be said. The existing methods, the methods which are commonly employed, are somewhat conventional in their character, and need exhaustive scrutiny. They are not sufficiently varied in their details to eliminate all danger of constant or cumulative errors, and new lines of attack, new points of view, ought to be considered and developed.

At present, the data relative to atomic weights are treated like successive links in a series of chains, each link to be considered separately; while in reality they form an interlacing network of interdependent quantities which should be discussed in some broadly general way.

To illustrate my meaning, let us consider a specific ratio,—

$$CaF_2 : CaSO_4,$$

which has been repeatedly measured in order to determine the atomic weight of fluorine. In this case a series of measurements is made, involving of necessity some error which may be great or small. From these data the atomic weight in question is computed, with the assumption that the atomic weights of calcium and sulphur are known. But these antecedent values are themselves in error by small but unknown amounts, and these errors are superimposed upon the experimental error of the ratio itself, so that all three appear in the final result of the calculation. The errors may be compensatory in part, or they may be cumulative; and which is the case we cannot certainly know. In a proper reduction of the data the ratio should contribute to our knowledge of all three of the atomic weights represented, and its error should be distributed among them instead of being piled, with others, upon one. That is, the ratio should not be discussed by itself, but should be combined with other ratios in such a manner that several related atomic weights might be determined simultaneously. This, I believe, will be the method of the future; and ultimately all trustworthy evidence, concerning all atomic weights, will be put into one set of normal equations with simultaneous solution for all. First, the experimental errors will be made as small as possible; after that they will be so uniformly distributed as to become inappreciable. For this procedure the mathematical method is well known, but the existing data are too incomplete for its present application. The final reductions will not be possible for many years to come. Work, comparable with that of Stas and Morley, needs to be done for all the chemical elements, and done with a broad purpose in view; after that, the mathematician can contribute his share to the solution of the general problem.

It is greatly to be hoped that at some future time some of the great laboratories may undertake systematic work of the kind I have indicated. The fundamental constants of chemistry are surely of equal importance with the value of the ohm, the form of the earth, or the solar parallax; and institutions like the Reichsanstalt in Berlin, the International Bureau of Weights and Measures at Paris, or the Davy-Faraday Laboratory of the Royal Institution, might well contribute to their determination. In this direction an international committee could exert an influence far beyond that of any individual, or even of any one society, but the problems at issue must first be clearly understood and formulated. To clear the ground, to arouse interest, and to stimulate systematic research, are important functions of the proposed body.

Yours very truly,

F. W. Clarke.

ATOMIC WEIGHTS.*

By Professor W. A. TILDEN, F.R.S.

The question of atomic weights has two aspects, the theoretical and the practical. For the purposes of theory we require to know the relative values of the atomic weights of all the elements with the utmost possible accuracy, with the object chiefly of explaining observed relations and discovering new ones. The true significance of the periodic scheme of arrangement will never be discovered till the atomic weights of a much larger number of elements are known more correctly than at present. And the employment of numbers which only roughly approximate to the true values for the atomic weights has led in the past to a large amount of speculation and discussion, of which nearly the whole is fruitless, because of necessity successive hypotheses have had to be put aside as knowledge of the subject has advanced, and numbers less inaccurate have been gradually substituted. This is true not only of such crude hypotheses as that of Prout, but of ideas proposed in more recent times concerning the relations of the several series in Mendeleeff's table.

Other questions have arisen, such as the possibility of the variation of the atomic weights within certain limits, but they only serve to illustrate the extreme difficulty of the subject in its present position; for while the facts are about equally well known to all chemists who have studied it, they have led some to consider variation possible, while others upon the same evidence are convinced that it is impossible. Unfortunately the settlement of such questions is still far off, for the complete series of determinations of all the elements made with a degree of accuracy comparable with that which has made the work of Stas famous is not to be expected in the present generation.

Another subject which has been re-opened by the action of the distinguished Committee of the German Chemical Society relates to the unit to be adopted. The practice which has prevailed universally since the time of Berzelius —that is, for nearly three-quarters of a century—of expressing the atomic weights in terms of hydrogen (H = 1) is now abandoned by the Committee in favour of the new scale, in which oxygen is the standard and O = 16. The considerations which have influenced the several members of the Committee are chiefly three, namely, first, the uncertainty still supposed to attach to the ratio H : O, though this is now as accurately known as it is likely to be; secondly, the fact that the atomic weights of many elements may be deduced directly from the composition of their compounds with oxygen, but less frequently from compounds with hydrogen; thirdly and chiefly, because

* Read before the British Association (Section B), Dover Meeting, 1899.

the oxygen scale brings many atomic weights very near to whole numbers. It is evident that this consideration is one which concerns alike the analyst, the student, and the investigator in every analytical operation, and in all circumstances which do not involve the discussion of the numerical interrelations of the atomic weights. For that purpose the H=1 scale will always be preferable, until an element is discovered having a smaller atomic weight than hydrogen, and of that there is at present no indication so far as terrestrial chemistry is concerned.

On the whole, the proposal of the German Chemical Society is probably the best solution of the difficulty. The scale in which O=16, however, implies the value 1·01, approximately, for hydrogen, and though it is true that for common analytical use the neglect to recognise this value will not lead to very serious consequences, it must be remembered that an appreciable error will be evolved in expressing the composition of compounds which are comparatively rich in hydrogen, such as the chief hydrocarbons and their derivatives. For C_5H_{12}, for example, the percentage of hydrogen is 16·66 or 16·80, according to the value assigned to the atomic weight of hydrogen.

But supposing the O=16 scale to be generally adopted, it is still highly desirable that there should be an understanding among the several Chemical Societies, and if possible among the members of these societies, as to the numbers to be chosen for ordinary use. Are we to use 27·1 for Al, 137·4 for Ba, 208·5 for Bi, 79·96 for Br, 35·45 for Cl, 52·1 for Cr, 126·85 for I, 206·9 for Pb, 24·36 for Mg, 200·3 for Hg, 14·04 for N, 194·8 for Pt, 39·15 for K, 23·05 for Na, 32·06 for S, &c., instead of the nearest whole numbers as has been customary in all these cases, with one exception, namely, chlorine? The temptation will be great, especially when we become aware that in the majority of cases the error introduced will be less than the ordinary experimental error. The example of platinum at once presents itself, without concerning yourselves about the special value for this element used by the potash makers for reasons of their own. But comparing the result of employing the old rounded off numbers with that of using the more exact values calculated on the O=16 scale, it is interesting to see how little is the effect on the percentage composition of potassium platinochloride deduced from the formula.

	Percentages calculated from—		Difference.
	K=39·15, Pt=194·8, Cl=35·45.	K=39, Pt=195, Cl=35·5.	
Potassium ..	16·118	16·049	0·069
Platinum . ..	40·099	40·123	0·024
Chlorine	43·783	43·827	0·044
	100·000	99·999	

There are some chemists to whom anything short of scientific accuracy is distasteful. It would be interesting to know whether in their daily work they use, for example, the number 14·04, instead of 14 for nitrogen, and what is the extent of experimental error they admit in analyses of nitrates or ammonia salts, of nitro compounds, or of organic matters by Kjeldahl, or any other recognised process. The composition of nitro-benzene may be used as an illustration. The percentage of N derived from the formula when C=12, H=1, N=14, O=16 is 11·38; while if C=12, H=1·01, N=14·04, and O=16, the result is 11·40, a difference of 0·02 per cent.

It is also usually forgotten that the values arrived at in all the best determinations of atomic weights are obtained under conditions which cannot be observed in daily laboratory practice, the weights, for example, being usually reduced to a vacuum standard. Hence the adoption of the numbers regarded as the most exact does not necessarily contribute to the exactness of ordinary analytical operations, however carefully performed.

A little common sense is required in all such matters, but it should be the common sense of the chemical world, and not the diverse fancies of individuals, and uniformity of practice would tend greatly to the general convenience. The only chance of arriving at such uniformity is to submit the question to discussion first at such meetings as those of the British Association and the Chemical Society, and subsequently at an international gathering such as it is proposed to hold in Paris next year. On such grounds I support cordially the chief proposals brought forward in the communication from Professor F. W. Clarke.

ON THE CHLOROBROMIDES OF LEAD.

By V. THOMAS.

In previous articles I have shown that chloride of lead was capable of giving with the iodide a well defined mixed salt, PbICl (*Bull. Soc. Chim.*, vol. xix., p. 488, 1898), and that the bromide treated in the same manner also led to the formation of a very homogeneous crystallised substance corresponding to the formula $3PbCl_2,PbBr_2$. The attack of the chloroiodised compound by peroxide of nitrogen is effected with the greatest facility, and thus allows the fact of its chemical existence to be easily demonstrated. The application of this method to the study of the chlorobromide does not lead to any result; the peroxide of nitrogen is not, in fact, able to displace the bromised quantitatively even at a high temperature.

Bromide and chloride of lead, both crystallise in the same system, and the formation of mixed isomorphous salts containing variable proportions of chlorine and of bromine might here occur, and cause some doubt as to the chemical personality of the compound $3PbCl_2,PbBr_2$. Thus, following my researches, I carried out with great care the determinations of the halogens in the products deposited at various temperatures.

This determination was carried out on the bodies deposited after the preparation of $3PbCl_2,PbBr_2$ at every 10°, from 60° to about 20°. Further, by the aid of titrated solutions I was able to constantly follow the variation in composition of the deposits between known temperatures.

The following are the results of some quantitative estimations:—

Part deposited below 60°.	Cl per cent.	Br per cent.
Between 60° and 50°	17·82	13·42
,, 50° ,, 40°	17·58	13·51
,, 40° ,, 30°	17·90	13·29
,, 30° ,, 20°	17·73	13·43

Theory requires for $3PbCl_2,PbBr_2$, Cl = 17·79, Br=13·37%. To follow the phenomenon between any two temperatures, such as 50° to 40° for example, we take at each intermediate degree of temperature a certain quantity of the substance deposited; this is then dissolved in water containing a small quantity of nitric acid; a known quantity of nitrate of silver (more than enough to precipitate all the halogens) is added to the solution; the excess of nitrate of silver is then titrated by means of sulphocyanide. In following this method, which is fairly rapid, we are able to see that the total amount of halogens contained in the precipitate is the same at each instant. If the compound $3PbCl_2,PbBr_2$ had not a definite chemical existence, but represented only an isomorphous mixture of the chloride and the bromide, the chemical composition of such a mixture, between sufficiently wide degrees of temperature, should oscillate between two limits of composition. It is the constancy of the composition of the product contained which causes me to be of the opinion that this chlorobromide has a definite composition.

I was able to obtain another mixed compound of chloride and bromide of lead by using the property possessed by bromine of displacing iodine from most of its metallic compounds. Thus in treating the chloroiodide of lead

PbICl by a current of bromine this latter takes the place of the iodine, giving the chlorobromide PbBrCl. This substitution is further effected at only a slightly elevated temperature, and the chlorobromide thus obtained retains the form of the chloroiodide which has served for its preparation. When slightly heated it melts, giving a liquid having a pale yellow colour, and which on cooling takes the form of a crystalline mass.

The synthetical and analytical results are as follows:—

I. *Synthesis.*—PbICl + Br = PbBrCl + I.

	Found.	Calculated.
Loss of weight	12·9	12·7
Iodine disengaged	34·01	34·46

II. *Estimation of the Lead and the Halogens in* PbBrCl.

	Found.	Calculated.
Pb	63·97	64·07
Br	25·23	24·88
Cl	10·92	11·05

The properties of this chlorobromide are the same as those of the compound previously described.

It does not appear to be affected by light; water dissolves it with decomposition; hydrochloric and hydrobromic acids act in the same manner, giving the corresponding haloid salts; nitric acid, either pure or charged with nitrous vapours, also attacks it very rapidly.

Glacial acetic acid does not dissolve it; alcohol at 95° only dissolves it in very small quantities, even when boiling; chloroform has no action at all.

When treated with fuming hydriodic acid it gives iodide of lead; after a sufficient time the transformation is complete.

In a forthcoming note I shall describe the double compounds of bromide and iodide of lead.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 11.

ON THE

MANUFACTURE OF NITRITE OF SODA.

By M. A. DARBON.

Details of the manufacture of nitrite of soda are very scarce in chemical literature; it will therefore be of interest to briefly describe the production of this substance, which is now very widely used in the dyeing industry. The raw material used in its manufacture consists of purified Chili saltpetre, and although the presence of sodic chloride may interfere with the value of the nitrite, the re-crystallisation of commercial saltpetre, with a view to the elimination of the sodic chloride, is not practised, as the expenses connected with the operation would be too great.

The saltpetre is melted in large cast-iron vessels, an operation which includes the evaporation of the hygroscopic water, and the decomposition of a part of the iodides and iodates which accompany the saltpetre. At 310° saltpetre begins to fuse, and before adding the lead necessary for its decomposition the temperature is raised to about 400—420°.

The lead should be as pure as possible, as the presence of small quantities of other metals might cause the decrepitation of the whole charge; it is, above all, antimony which is the most to be feared; the lead used must be in thin sheets. About 280 parts of lead are necessary for 100 parts of saltpetre. As soon as the melted saltpetre has reached the desired temperature the necessary quantity of lead is gradually added; at the same time the whole must be kept constantly stirred so as to obtain a very intimate mixture. It is necessary to carefully watch that the charge does not become too strongly heated, for fear the vessel might be pierced; in case of emergency, to prevent such an accident, a quantity of cold saltpetre must be added, or the fire withdrawn. When all the lead has been added the stirring must still be kept up for some time, and the melted mass is then removed by means of a large cast-iron ladle. It is then run in the form of fine threads into cold water in which its solution is helped by constant stirring. The decomposition of the saltpetre by the lead at 420—500° has the effect of producing, besides the nitrite, about 1 per cent of caustic soda, which dissolves a certain quantity of the oxide of lead formed; this latter should also be removed. This is generally effected by neutralising with nitric acid; in this manner saltpetre is re-formed, while the oxide of lead is precipitated in the state of insoluble hydroxide. We may also use nitrate of lead or sulphuric acid for neutralising the solution; sulphuric acid is preferable on account of its low price, but we then obtain sulphate of soda, which is deposited in the concentrating vessels in the form of the anhydrous salt. We thus have in aqueous solution nitrite, undecomposed saltpetre, caustic soda holding oxide of lead in solution, and the soluble impurities of the saltpetre, such as chloride of sodium, &c. The insoluble residue consists of oxide of lead, a very small quantity of metallic lead, which has escaped oxidation, and a certain proportion of peroxide of lead. The solution diluted to about 6—8° Baumé is neutralised with nitric acid (or dilute sulphuric acid, or again with a solution of nitrate of lead); the oxide of lead in solution is precipitated, and the addition of the acid is continued as long as a precipitate is formed.

We may here correct an error which has slipped into most treatises on chemistry; most authors state that nitrite of sodium has an alkaline reaction, but this is not the case—the pure nitrite is absolutely neutral.

The neutralised solution separated from the insoluble residue by any convenient method is concentrated in cast-iron basins until it reaches 42—45° Baumé when warm.

The insoluble residue is thrown on a large filter of coarse material, such as sacking, washed with warm water, and the wash-waters added to the principal solution. The residuary oxide of lead is capable of various applications, which will be dealt with directly. The concentrated solutions are added together in cast-iron vats and left to crystallise; if the crystals thus obtained are not pure they must be re-dissolved and re-crystallised. The pure crystals are separated in a centrifugal machine, washed, dried, and packed.

The desiccation takes place in an oven, the temperature of which is carried to about 50°, and the crystals are packed in cylinders of double thicknesses of parchment paper.

The residuary oxide of lead may be either melted and cast as it is, reduced to the metallic state, or transformed into minium; it can also be used for the preparation of white-lead, of nitrate, acetate, or other plumbic compounds.

The analysis of the nitrite is generally made with a titrated solution of permanganate of potassium. By dissolving 9·594 grms. of permanganate in 1 litre of water we obtain a solution, each c.c. of which is equal to 1 centigrm. of nitrite of sodium.

The analysis is carried out in the following manner:—A known quantity of the nitrite is rapidly weighed and dissolved in an Erlenmeyer flask of 150—200 c.c. capacity with about 80 c.c. of water. To this solution are added a few c.c. of dilute sulphuric acid (1:4), and it is then titrated. When the colouration begins to disappear with difficulty, a fresh quantity of sulphuric acid, much stronger than the last, is added, as there is now no longer any danger of nitrous acid escaping. The addition of the permanganate is continued drop by drop until the rose tint is permanent for about a quarter of an hour.

To hasten the final reaction the solution may be heated towards the end of the operation to 30—40°. The analysis of the melted mass is carried out in the same manner as is that of the oxide of lead to see if the washing was thoroughly done.—*Chemiker Zeitung*, 1899, p. 173.

CORRESPONDENCE.

DETERMINATION OF CARBON IN IRON AND STEEL WITHOUT COMBUSTION APPARATUS.

To the Editor of the Chemical News.

Sir,—May I call the attention of those interested to a few points in the process Mr. Dougherty has described (Chem. News, lxxx., 121) for the estimation of carbon in steel?

The fact that the method is not so novel as seems to be imagined might well be overlooked if it were not that the claims made for it are occasionally exaggerated, and the data for the calculation is at variance with that of other experimenters.

Papers on similar lines, usually claiming the process as an approximate one, must be known to most chemists actually engaged in iron analysis; the statement, however, that "the method seems to be fully equal to the elaborate standard combustion process, and has the advantage of being simpler and quicker, with fewer possible sources of error," may well be taken exception to. The greater simplicity may be admitted; the greater rapidity is less obvious, since both processes are alike except in the manner of burning the carbon; the greater freedom from error must be emphatically denied, because, apart from errors inherent in the process, the presence of the not uncommon elements chromium and tungsten would invalidate it altogether.

I can hardly imagine anyone at all familiar with the literature of iron and steel analysis assuming that the residue from the treatment with the double copper salt solution was pure carbon. Mr. Dougherty's countryman, Blair—who by the way calls attention to a similar process in his Chemical Analysis of Iron—finds the carbonaceous residue to be $(C_{50}H_{21}ClO_{15})_3NO_2$. Schützenberger and Bourgeois reckon it to be $C_{11}H_6O_3$, and Zaboudsky—after liberating the carbon by solutions of copper or silver, or mercury salts—writes its composition $C_{12}H_6O_3$, and prepares organic derivatives therefrom. Calculated from either Schützenberger's or Zaboudsky's formula, the percentage of carbon is over 70. Blair says the residue contains about 70 per cent of carbon. Mr. Dougherty's figure is 67·5.

In one respect Mr. Dougherty's procedure is, so far as I am aware, certainly original. The carbonaceous residue is washed four times with hot nitric acid. Zaboudsky says the residue is soluble in warm nitric acid, and this is true, in a lesser degree, even at the dilution used by Mr. Dougherty.

Boussingault, who seems to have initiated the indirect estimation of carbon on the above principle, determines both combined carbon and graphite in the residue from the same example. (See Chem. News, 1870, xxii., 317).—I am, &c.,

Harry Brearley.

Addendum.—The vision conjured up by the phrase "the elaborate standard combustion process" will generally accord with the descriptions given of it in text-books, which by no means truly represent the unadorned process as carried out in a busy iron works' laboratory. Except that the apparatus is rather bulky, there is nothing elaborate about the dry combustion process. It is merely a heated tube suitably packed, having a KHO wash-bottle at one end, and a $CaCl_2$ drying tube and weighed absorption bulb at the other. A supply of oxygen is not indispensable, and the boats may be taken in and out of the hot tube. Thus in a stream of air the dried carbonaceous residues are successively burnt each twenty minutes. A similar procedure is, I believe, practised extensively where all varieties of steel are analysed, and the agreement with the most carefully conducted combustions is remarkable.

Some time ago there was occasion to determine whether the sometime unavoidable rapid evolution of gas during direct combustions with lead peroxide was more than the KHO bulbs and the attached $CaCl_2$ tube could cope with; the following experiments were therefore made:—

An aspirator, having constant suction, drew 2¼ litres of air through the furnace and a KHO bulb in eight minutes. The $CaCl_2$ tube belonging to the bulb held only 2 inches of $CaCl_2$, yet the loss through imperfect dehydration was only 0·00175 grm. The same bulb was attached to the furnace, the carbonaceous residue from 5 grms. of steel was kept in the tube at full red heat for five minutes, then the current of air passed at the same rate as before. The increased weight of the bulb calculated to 1·17 per cent carbon; numerous previous determinations have fixed the percentage at 1·18. Thus the absorption of the CO_2 was nearly perfect, although the gas passed about ten times faster than text-book rate.

Taken all in all, and particularly when steels containing special elements are daily dealt with, there are few processes that combine speed and accuracy more satisfactorily than dissolving in a copper solution by means of a mechanical shaker and dry combustion of the residue: certainly Dougherty's is not one.

September 11, 1899.

THE 32 EQUIVALENT AND ITS RELATION TO THE PERCENTAGE OF AVAILABLE SODA IN CAUSTIC SODA.

To the Editor of the Chemical News.

Sir,—I have been out of Chicago since writing my last letter, and have only recently had the opportunity of reading Mr. Pattinson's letter dated May 24th replying to mine.

With regard to Mr. Pattinson's opening statement, I would say I do not claim to have quoted his exact words.

Mr. Pattinson's criticisms upon my method of calculation appear to me justifiable, and unless an acid is truly normal the principle of equivalents cannot be applied to it.

It would therefore appear that, as the "Tyne test" was originated by the assumption that the atomic weight of sodium was 24, it will be necessary to prepare an acid which will saturate 41 grms. NaHO per litre in order to get correct results for caustic soda on this basis. Of course, an arbitrary calculation might be made with the acid prepared to give correct results with sodium carbonate.—I am, &c.,

H. A. Hooper.

Chicago, Ill., U.S.A., August 5, 1899.

The South Western Polytechnic.—The operations of this Institute are divided into two distinct portions:—Day Classes for both Men and Women, and Evening Classes. The latter offer to artizans and others engaged in technical and commercial industries the means of instruction in Applied Science and Art. The Institute is lighted throughout by electricity, and provided with well-equipped Mechanical, Electrical, Physical, Chemical, and Biological Laboratories, with Art and Photographic Studios, and with Workshops. It is directed by a Governing Body, consisting of representatives of the City Parochial Charities, the London County Council, the London School Board, and the Chelsea Vestry. The whole is under the supervision of the Principal, Prof. Herbert Tomlinson, B.A., F.R.S., assisted by the many Professors, Lecturers, Demonstrators, and Instructors, which the extensive list of studies necessitates. The new Session commences on Monday, September 25th.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 8, August 21, 1899.

Decomposition of Monomanganous Phosphate at 0° and at 100°.—Georges Viard.—It has been known for some time that monomanganous phosphate, $(PO_4)_2MnH_4+2H_2O$, is decomposed both by hot and cold water. Cold water gives a crystalline precipitate of di-manganous phosphate, $(PO_4)_2Mn_2H_2+6H_2O$, whilst hot water gives a crystalline precipitate, $(PO_4)_2Mn_2H_2+(PO_4)_2Mn_3+4H_2O$, which is intermediate between the di- and tri-manganous phosphate, and sometimes called ditrimanganous phosphate. The author has studied these reactions quantitatively. The method employed is that of Gibbs, which in this case is particularly useful, since the liquid always contains more than double the quantity of phosphoric acid necessary to form ammonia-manganous phosphate. The results are shown on a curve.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxi., No. 7.

On the Hydrosulphites of Ammonium.—Maurice Prud'homme.—Already inserted in full.

On a New Mineral: Carnotite.—C. Friedel and E. Cumenge.—Already inserted in full.

Action of Acetate of Lead in Acetic Solution on Chloride of Benzylidene and Chloride of Benzenyl.—F. Bodroux.—The author has endeavoured to prepare acetate of benzylidene by a similar method to that used for preparing acetic ethers. For this purpose he dissolves 35 grammes of litharge in 80 grms. of acetic acid, and having added 20 grms. of chloride of benzylidene he carried the whole to boiling-point. A violent reaction commenced immediately; the flame was then withdrawn, but the reaction continued for some little time. When it ceased, he boiled up again for ten minutes; then, after cooling, he filtered and drove off about three-quarters of the acetic acid by distillation. The residue, treated with a cold dilute solution of potash, gave about 20 grms. of an oily liquid, which, after decanting and washing with water, was dissolved in ether; the dried solution was allowed to stand. On evaporation, the product of the reaction, which possessed a strong smell of bitter almonds, crystallised slowly and partially in colourless plates, melting, without decomposition, at 45—46°.

Phenylhydrazinic Compounds of Metallic Hyposulphites, Hyposulphates, and Hypophosphites.—J. Moitessier.—Phenylhydrazine forms—the same as does ammonia—crystallised compounds with the hyposulphites, hyposulphates, and the hypophosphites of the metals of the magnesium series. The author here describes the preparation and properties of phenylhydrazinic hyposulphite of cadmium, $S_2O_3Cd.2(C_6H_5.N_2H_3)$; phenylhydrazinic manganous hyposulphate, $S_2O_6Mn.5(C_6H_5.N_2H_3)$; phenylhydrazinic hypophosphite of zinc,—

$$(PO_2H_2)_2Zn.2(C_6H_5.N_2H_3);$$

and phenylhydrazinic hypophosphite of nickel,—

$$(PO_2H_2)_2Ni.2(C_6H_5.N_2H_3).$$

Other salts of the metals of the magnesium series, such as the selenates, pyrophosphates, and the borates, also give phenylhydrazinic compounds. Further, by working at a low temperature and in alcoholic solution, the author has obtained a compound of phenylhydrazine and nitrate of silver; it is, however, very unstable at the ordinary temperature.

MISCELLANEOUS

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) at the Dover Meeting of the British Association:—

President—Horace T. Brown, LL.D., F.R.S.

Vice-Presidents—Prof. H. E. Armstrong, F.R.S.; Prof. P. Frankland, F.R.S.; Prof. A. Ladenburg; Prof. F. R. Japp, F.R.S.; Prof. R. Fittig.

Secretaries—A. D. Hall, M.A.; C. A. Kohn, Ph.D. (Recorder); T. K. Rose, D.Sc.; Dr. W. P. Wynne, F.R.S.

Committee—A. H. Allen; Sir William Roberts-Austen, K.C.B.; Sir William Crookes, F.R.S.; Prof. H. B. Dixon, F.R.S.; Ludwig Mond, F.R.S.: J. H. Gladstone, F.R.S.; W. H. Pendlebury; Prof. J. Emerson Reynolds, F.R.S.; Sir Henry E. Roscoe, F.R.S.; T. E. Thorpe, F.R.S.; W. A. Tilden, F.R.S.

The Papers brought before the Section were as follows:—

President's Address—The Assimilation of Carbon by the Higher Plants.

Prof. Dewar—The Solidification of Hydrogen.

Report of the Committee on Preparing a New Series of Wave-length Tables of the Spectra of the Elements.

Report of the Committee on the Continuation of the Bibliography of Spectroscopy.

Report of the Committee on the relation between the Absorption Spectra and Chemical Constitution of Organic Substances.

Report of the Committee on Isomeric Naphthalene Derivatives.

Discussion on the Laws of Substitution, especially in Benzenoid Compounds—Prof. H. E. Armstrong.

Prof. H. E. Armstrong—The relative Orienting Power of Chlorine and Bromine.

Prof. H. E. Armstrong—Isomorphism in Benzenesulphonic Derivatives.

H. J. H. Fenton—Oxidation in presence of Iron.

H. J. H. Fenton and H. Jackson—The Condensation of Glycollic Aldehyde.

Prof. J. Emerson Reynolds—Some New Silicon Compounds.

Report of Sewage Committee.

Prof. F. Clowes—The Bacterial Treatment of Sewage.

W. Scott-Moncreiff—The Place of Nitrates in the Biolysis of Sewage.

Prof. Hanriot—The Excretory Products of Plants.

Prof. Marshall Ward, Dr. A. Calmette, and Prof. H. E. Armstrong—Symbiotic Fermentation.

Report of the Committee on the Teaching of Natural Science in Elementary Schools.

Discussion on Atomic Weights—Prof. F. W. Clarke and Prof. Tilden.

Prof. A. Ladenburg—The Development of Chemistry in the last Fifteen Years.

W. J. Pope—The Influence of Solvents upon the Optical Activity of Organic Compounds.

T. S. Dymond—The Chemical Effect on Agricultural Soils of the Salt Water Flood of November 29th, 1897, on the East Coast.

Dr. J. H. Gladstone and W. Hibbert.—Phenomena connected with the drying of Colloids: mineral and organic.

Dr. A. Fernbach.—The Influence of Acids and of some Salts on the Saccharification of Starch by Malt-diastase.

Dr. G. H. Morris—Note on the Combined Action of Diastase and Yeast on Starch Granules.

Dr. G. H. Morris.—On the Action of Acids on Starch.

R. S. Morrell and J. M. Crofts.—The Action of Hydrogen Peroxide on Carbohydrates in presence of Iron Salts.

Dr. M. O. Forster.—The Influence of Substitution on Optical Activity in the Bornylamine Series.

Dr. M. O. Forster.—New Derivatives from Camphoroxime.

Dr. C. A. Kohn and Dr. W. Trantom.—The Action of Caustic Soda on Benzaldehyde.

Col. J. Waterhouse.—Note on the Action of Light upon Metallic Silver.

Prof. W. R. Hodgkinson, Capt. Waring, and Capt. Desborough.—Some experiments to obtain definite Alloys of Cadmium, Zinc, and Magnesium with Platinum and Palladium.

Prof. W. R. Hodgkinson and Capt. Leaky—Action of Acetyl and Benzoyl Chlorides on Copper Sulphate

Prof. W. R. Hodgkinson and Lieut. W. H. Welby-Thorpe—The Reaction between Potassium Cyanide and Metadinitrobenzene.

Prof. W. R. Hodgkinson and Messrs. Seton and Stevenson—The Composition of Brown Powder Residue.

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THE CHEMICAL NEWS.

Vol. LXXX., No. 2079.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Dover, 1899.

By HORACE T. BROWN, LL.D., F.R.S.,
President of the Section.

(Concluded from p. 142).

If instead of taking the air from a height of three or four feet from the ground, we examine the stratum only one or two centimetres above the surface of a soil free from vegetation, we find, as might be expected, a very large increase in the amount of carbon dioxide, which may exceed, under these circumstances, 12 or 13 parts per 10,000 of air. Such a soil, in fact, gives off by diffusion into the surrounding air an amount of carbon dioxide which is comparable to that evolved by a respiring leaf; that is to say, about 50 c.c. per square metre per hour. This is probably a factor which has to be taken into account in considering the assimilative power of vegetation of very low growing habit, but in all other cases we may assume with safety that aërial plants have to take in their carbon dioxide from air in which its tension does not exceed $\frac{1}{10000}$ of an atmosphere.

The actual intake of carbon dioxide is determined by enclosing the entire leaf in specially constructed air-tight glazed cases, through which a sufficiently rapid air stream is passed. These cases are so arranged that the leaf can be enclosed whilst still attached to a plant which is growing out in the open under perfectly natural conditions, and some of them are sufficiently large to take the entire leaf of a sunflower.

The carbon dioxide content of the air is determined both before and after its passage through the apparatus; and since the amount of air passed is known, we have all the data requisite for determining the actual amount retained by the leaf.

An experiment generally lasts from five to six hours, and the carbon dioxide fixed in this time may amount to 150 c.c. or more, the actual error of determination being very small indeed.

For purposes of comparison the volumes are reduced to the actual number of cubic centimetres of the gas absorbed by a square metre of leaf in one hour, which of course necessitates an exact determination of the area of the leaf. This is most conveniently effected by printing the leaf on sensitised paper, and tracing round its outline with a planimeter set to read off square centimetres; a far more accurate and expeditious plan than that of cutting out a fac-simile of the leaf from paper of a known weight per unit of area.

If it is desired to estimate the assimilative power of a leaf in an atmosphere artificially enriched with carbon dioxide, the air stream before entering the leaf case is passed through a small tower containing fragments of marble, over which there drops a very slow stream of dilute acid, whose rate of flow is so proportioned to the air stream as to give about the desired enrichment with carbon dioxide. The stream of air is then divided, one part going on directly to the leaf case, whilst the other passes through a separate absorption apparatus and meter for the accurate determination of its carbon dioxide content.

In order to show the kind of results obtained in this manner I will give one or two examples.

A leaf of the sunflower, having an area of 617·5 sq. c.m., was enclosed in its case whilst still attached to the plant, and was exposed to the strong diffuse light of a clouded sky for five and a half hours, air being passed over it at the rate of nearly 150 litres per hour. The content of the air in carbon dioxide as it entered the apparatus was 2·80 parts per 10,000, and this was reduced to 1·74 parts per 10,000 during its passage over the leaf. This corresponds to a total absorption of 139·95 c.c. of carbon dioxide, or to an intake of 412 c.c. per square metre per hour. If we assume that the average composition of the carbohydrates formed is that of a $C_6H_{12}O_6$ sugar, the above amount of carbon dioxide corresponds to the formation of 0·55 grm. of carbohydrate per square metre per hour. But we must bear in mind that the average tension of the carbon dioxide in the leaf case was only equal to 1·93 parts per 10,000—that is, only about seven-tenths of its tension in the normal air. A correction has therefore to be made if we wish to know how much the leaf would have taken in, under similar conditions of insolation, if it had been bathed with a current of air of sufficient rapidity to practically keep the amount of carbon dioxide constant at its normal amount of 2·8 per 10,000. We shall see later on that, well within the limits of this experiment, the intake is proportional to the tension, so that, applying this correction we may conclude that under identical conditions of insolation and temperature this leaf would have taken in an amount of carbon dioxide from the free air at a rate sufficient to produce 0·8 grm. of carbohydrate per square metre per hour. This is almost exactly equal to the assimilation rate of the sunflower which I deduced in 1892 from the indirect process of weighing equal areas of the leaf lamina before and after insolation, and it also agrees fairly well with some of Sachs's original experiments of a similar nature.

In another experiment made with the leaf of *Catalpa bignonioides* in full sunlight the amount of carbon dioxide in the air passing over the leaf fell from 2·80 to 1·79 parts per 10,000, the total hourly intake for the square metre being 344·8 c.c. When this is corrected for tension it corresponds to an assimilation in free air of 0·55 grm. of carbohydrate per square metre per hour.

An increase in the intensity of the daylight, as might be expected, influences to some extent the rate of intake of atmospheric carbon dioxide; but providing the illumination has reached a certain minimum amount, a further increase in the radiant energy incident on the leaf does not result in anything like a proportional amount of assimilation. We have found, for instance, that the rate of assimilation of a sunflower leaf, exposed to the clear northern sky on a warm summer's day, was about one-half of what it was when the leaf was turned round so as to receive the direct rays of the sun almost normal to its surface. Now in this latter case the actual radiant energy received by the leaf was at least twelve times greater than was received from the northern sky, but the assimilation was only doubled.

These differences in the effect of great variation of illumination become still less marked when we use air which has been artificially enriched with carbon dioxide. In one instance of this kind, for example, we found the assimilation in the full diffuse light of the northern sky to be 87 per cent of what it was in direct sunshine.

This brings me to another interesting point on which I have already touched slightly—the enormous influence which slight changes in the carbon dioxide content of the air exert on the rate of its ingress into the assimilating leaf.

With a constant illumination, either in direct sunlight or diffuse light, the assimilatory process responds to the least variation in the carbon dioxide, and within certain limits, not yet clearly defined, the intake of that gas into the leaf follows the same rule as the one which holds good with regard to the absorption of carbon dioxide by a freely exposed surface of a solution of caustic alkali; that is to say, from air containing small but variable quantities of carbon dioxide *the intake is directly proportional to the tension of that gas.*

A single experiment will be sufficient to illustrate this.

A large sunflower leaf, still attached to the plant, and exposed to a clear northern sky, gave an assimilation rate equal to 0·331 grm. of carbohydrate per square metre per hour, when air was passed containing an average amount of 2·22 parts of carbon dioxide per 10,000. When the experiment was repeated under similar conditions of illumination, but with air containing 14·82 parts of CO_2 per 10,000, the intake corresponded to an hourly formation of 2·409 grms. of carbohydrate per square metre. The ratio of the tensions of the carbon dioxide in the two experiments is 1 to 6·7 and the assimilatory ratio is 1 to 7·2, so that the increased assimilation is practically proportional to the increase in tension of the carbon dioxide.

Since an increase of carbon dioxide in the atmosphere surrounding a leaf is followed by increased assimilation even in diffuse daylight, it is clear that, under all ordinary conditions of illumination, the rays of the right degree of refrangibility for producing decomposition of carbon dioxide are largely in excess of the power of the leaf to utilise them. Under natural conditions this excess of radiant energy of the right wave-length must, from the point of view of the assimilatory process, be wasted, owing to the limitation imposed by the high degree of dilution of atmospheric carbon dioxide. But although the actual manufacture of new material within the leaf lamina is so largely influenced by small variations in the carbon dioxide of the air, we are not justified in concluding that the plant *as a whole* will necessarily respond to such changes in atmospheric environment, since the complex physiological changes involved in metabolism and growth may have become so intimately correlated that the perfect working of the mechanism of the entire plant may now only be possible in an atmosphere containing about three parts of carbon dioxide in 10,000.

We have commenced a series of experiments which will, I hope, throw considerable light on this point, but the work is not at present in a sufficiently advanced state for me to make more than a passing allusion to it.

The penetration of the highly diluted carbon dioxide of the atmosphere into the interior air spaces of the leaf on its way to the active centres of assimilation must, in the first instance, be a purely physical process, and no explanation of this can be accepted which does not conform to the physical properties of the gases involved.

Since there is no mechanism in the leaf capable of producing an ebb and flow of gases within the air spaces of the mesophyll in any way comparable with the movements of the tidal air in the lungs of animals; and since, also, the arrangement of the stomatic openings is such as to effect a rapid equalisation of pressure within and without the leaf, we must search for the cause of the gaseous exchange, not in any mass movement, but in some form of diffusion. This may take place in the form of *open diffusion* through the minute stomatic apertures, which are in communication both with the outer air and the intercellular spaces, or the gaseous exchange may take place through the cuticle and epidermis by a process of *gaseous osmosis*, similar to that which Graham investigated in connection with certain colloid septa.

For many years there has been much controversy as to which form of gaseous diffusion is the more active in producing the natural interchanges of gases in the leaf. The present occasion is not one in which full justice can be done to the large amount of experimental work which has from time to time been carried out in this direction. Up to comparatively recently the theory of cuticular osmosis has been the one which has been more commonly accepted, free diffusion through the open stomata being considered quite subsidiary. In 1895, however, Mr. F. F. Blackman brought forward two remarkable papers which opened up an entirely new aspect of the subject. After showing the fallacy underlying certain experiments of Boussingault, which had been generally supposed to prove the osmotic theory of exchange, Mr. Blackman gave the results of his own experiments with a new and beautifully constructed apparatus, which enabled him to measure very minute quantities of carbon dioxide given off from small areas of the upper and under sides of a respiring leaf, and also to determine the relative intake of carbon dioxide by the two surfaces during assimilation in air artificially charged with that gas. The conclusions drawn are that respiratory egress, and assimilatory ingress of carbon dioxide do not occur in the upper side of a leaf if this is devoid of stomatic openings, and that when these openings exist on both the upper and under sides the gaseous exchanges of both physiological processes are directly proportional to the number of stomata on equal areas; hence in all probability the exchanges take place only through the stomata.*

These observations of Mr. Blackman are of such far-reaching importance, and lead, as we shall see presently, to such remarkable conclusions with regard to the rate of diffusion of atmospheric carbon dioxide, that we felt constrained to inquire into the matter further, and for this purpose we employed a modified form of the apparatus which we have used throughout our work on assimilation. This was so arranged that a current of ordinary air could be passed, just as in Mr. Blackman's experiments, over the upper and lower surface of a leaf separately, the increase or decrease in the carbon dioxide content of the air being determined by absorption and titration in the manner I have already alluded to.

In this way we were able to employ comparatively large leaf areas, and to continue an experiment for several hours, so that we had relatively large amounts of carbon dioxide to deal with, and the ratios of gaseous exchange of the two sides of the leaf could consequently be determined with considerable accuracy.

Our results, on the whole, are decidedly confirmatory of Mr. Blackman's observations. The side of a leaf which is devoid of stomatic openings certainly neither allows any carbon dioxide to escape during respiration, nor does it permit the ingress of that gas when the conditions are favourable for assimilation. On the other hand, when stomata exist on both the upper and under sides of a leaf, gaseous exchanges take place through both surfaces, and, as a rule, in some sort of rough proportion to the distribution of the openings. There is, however, under strong illumination, a greater intake of carbon dioxide through the upper surface than would be expected from a mere consideration of the ratio of distribution of the stomata.† Nevertheless, the general connection between gaseous exchange and distribution of stomata is so well brought

* There is one important fact to be borne in mind when considering how far these observations exclude the possibility of cuticular osmosis. In the many leaves we have examined, Mr. Escombe and I have found that the occurrence of stomata on the upper surface of the leaf is always correlated with a much less dense palisade parenchyma. The cuticle and epidermis under these conditions are in a much more favourable state to allow carbon dioxide to pass into the leaf by osmosis than when the closely packed palisade cells abut against the epidermis, as they do when this is imperforate.

† Granted that the stomata constitute the paths of gaseous exchange, it is clear that the amount of diffusion through them, other things being equal, must depend very largely on the extent to which they are opened. The delicate self-regulating apparatus which governs the size of the openings is so readily influenced, amongst other things, by difference of illumination, that *à priori* we should not expect the stomata on the upper surface of an insolated leaf to be in the same condition as those of the more shaded lower surface. This may very well account for the stomatic ratio of the two sides not being in closer correspondence with the assimilatory ratios, as found in most of our experiments carried out in bright sunlight. In light of lesser intensity there is always a closer correspondence of the two ratios.

There is also another possible explanation of the fact. Since we have good reason to believe that the principal part of the assimilatory work is carried on by the palisade parenchyma, which occurs in the upper side of the leaf, the tension of the carbon dioxide in the air spaces of that part of the mesophyll is probably less than it is in the spongy parenchyma. There will, therefore, be a higher "diffusion gradient" between the carbon dioxide of the outer and inner air in the former case than in the latter, and this would certainly tend to a more rapid diffusion through the openings in the upper side of the leaf.

out that we must regard it as highly probable that these minute openings are the true paths by which the carbon dioxide enters and leaves the leaf.

We must now look at certain physical consequences which proceed from this assumption, and see how far they can be justified by the known or ascertainable properties of carbon dioxide at very low tensions.

The leaf of *Catalpa bignonioides* is hypostomatic, and therefore takes in carbon dioxide only by its lower surface. Under favourable conditions it is quite possible, during assimilation, to obtain an intake of atmospheric carbon dioxide into this leaf at the rate of 700 c.c. per square metre per hour (measured at 0° and 760 m.m.), corresponding to an average linear velocity of the carbon dioxide molecules of 3·8 *centimetres per minute*, supposing the intake to be distributed evenly over the whole of the lower leaf surface. This velocity is almost exactly one-half of that at which carbon dioxide will enter a freely exposed surface of a solution of caustic alkali. But if the intake of the gas is confined to the stomatic openings of the leaf, its velocity of ingress must be very much greater than this.

We have carefully determined the number of stomata occurring on a given area of this particular leaf, and also the dimensions of the openings, and find that the total area of the openings, supposing them to be dilated to the fullest possible extent, amounts to just under *one per cent* of the leaf surface. It follows from this that the average velocity of the atmospheric carbon dioxide in passing through these openings must be 380 *centimetres per minute* —that is to say, just *fifty* times greater than into a freely exposed absorbent surface of alkali. In other words, supposing every one of the stomatic openings of this leaf could be filled up with a solution of caustic alkali, the absorbent power of the leaf as a whole would only be $\frac{1}{50}$ of what it actually is when assimilating.

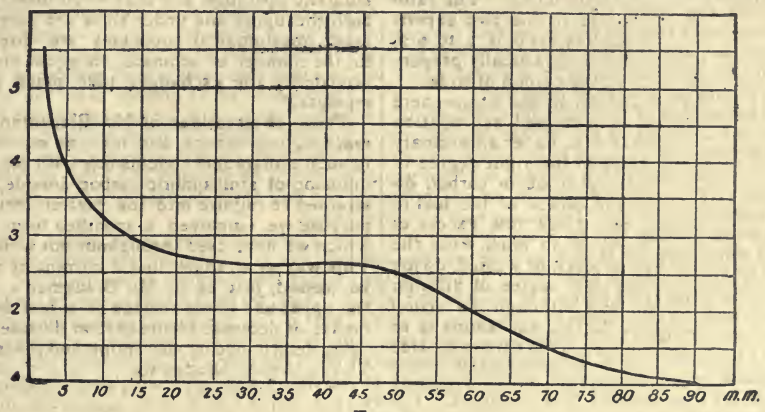

Fig. 1.

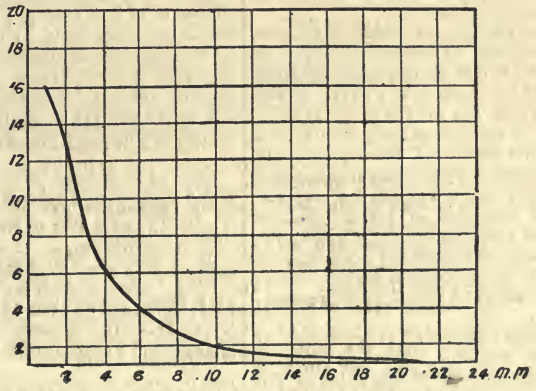

Fig. 2.

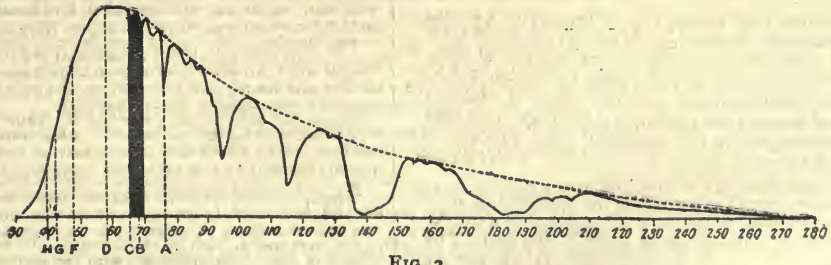

Fig. 3.

These are some of the consequences which flow from an acceptance of the hypothesis of stomatic exchange, and it appeared to be impossible to accept that hypothesis unreservedly without some collateral evidence that these comparatively high velocities of diffusion are physically possible when dealing with such low gradients of tension as must necessarily exist when the highest amount of carbon dioxide does not exceed 0·03 per cent.

The well-known general law expressing the rate of the spontaneous intermixture of two gases when there is no intervening septum, was, as everyone knows, established by Graham, and the more elaborate investigations of Loschmidt many years later served to confirm the general accuracy of this law, and to show that, within very narrow limits, the diffusion constant varies in different gases inversely as the square roots of their densities.

But a mere knowledge of the diffusion constants of air and carbon dioxide does not, as far as I can see, materially assist us in the particular case we have under consideration. In order to gain some idea of what is actually possible in the way of stomatic diffusion in an assimilating leaf we must know something of the *actual rate* at which atmospheric carbon dioxide can be made to pass into a small chamber containing air at the outside tension, but in which the carbon dioxide is kept down almost to the vanishing point by some rapid process of absorption; and we must also determine the influence of varying the size of the aperture through which the diffusion takes place.

Our attempts to answer these questions experimentally have led us into a long investigation, which promises to be of wider interest than we had first imagined. I only propose to give on this occasion a general account of the results so far as they affect the physical question of the intake of carbon dioxide into the plant.

When a shallow vessel containing a solution of caustic alkali is completely covered, the air above the liquid is very speedily deprived of the whole of its carbon dioxide. If we now imagine a hole to be made in the cover of the vessel, carbon dioxide will enter the air space by free diffusion, and its amount can be very accurately determined by subsequent titration in the manner I have previously referred to. The time occupied by the experiment and the dimensions of the aperture being known, we can express the results in actual amounts of carbon dioxide passing through unit area of aperture in unit of time; or, since the tension of that gas in the outer air is known, we can express the average rate of the carbon dioxide molecules across the aperture in terms of actual measurement, say centimetres per minute.

We have made a very large number of experiments of this kind, using, in the first instance, dishes of about 9 c.m. in diameter, and varying the size of the holes in the cover, the air space over the absorbent liquid being always the same.

The accompanying curve, Fig. 1, illustrates the effect which a gradually decreasing orifice has on the rate of diffusion of atmospheric carbon dioxide under these conditions. The diameters of the orifice in millimetres are given on the abscissa line, and the rates of diffusion through equal areas of the apertures are taken as ordinates, the rate of absorption in the open dish under similar conditions being taken as unity.

It will be seen that in the first instance a gradual reduction of the diameter of the opening is accompanied by a very regular increase in the rate of passage of the carbon dioxide until a diameter of about 50 m.m. is reached; that is to say, up to a point at which about two-thirds of the area of the dish is covered. A further progressive diminution in the size of the aperture makes comparatively little difference in the diffusion rate until we reach about 20 m.m., beyond which the curve again begins to rise, increasing rapidly in steepness as the apertures become smaller.

The experiments with open dishes are too crude for a study of the influence of very small apertures, so for this part of our work we constructed a special form of apparatus which has enabled us to determine the relative rates of diffusion through orifices in thin metal plates ranging down to 1 m.m. in diameter.

I have plotted the results of such a series of experiments (see Fig. 2), showing the relative rates of diffusion of atmospheric carbon dioxide through equal areas of apertures between 20 m.m. and 1 m.m. in diameter, under constant conditions, and it will be noticed how very steep the curve becomes after diameters of 5 or 6 m.m. are reached.

The speed at which the diffusion of atmospheric carbon dioxide takes place through unit area of an orifice of 1 m.m. in diameter is just sixteen times as fast as it is through unit area of an aperture of 20 m.m.; and since we know that the rate of passage in the latter case is two and a half times greater than the absorption rate of an equal area of a freely exposed surface of a solution of caustic alkali, we arrive at the conclusion that, under the particular conditions of our experiment, the diffusion rate through an aperture of 1 m.m. is *forty times* greater than the rate of absorption of a free alkaline surface of equal area.

This corresponds to an actual average rate of passage of the molecules of the atmospheric carbon dioxide of about 266 centimetres per minute.

Now, we have already seen, in the case of a Catalpa leaf, that if the gaseous exchange during assimilation goes on only through the stomatic openings, we require a minimum velocity of something like 380 centimetres per minute—a velocity which we are sensibly approaching in our experiments with apertures of about 1 m.m. in diameter. But the effective area of a stomatic opening of the Catalpa leaf is equal to that of a circle with a diameter of less than $\frac{1}{100}$ m.m., and since our experiments indicate a very rapid increase in the velocity of diffusion as the aperture is diminished, it is clear that no difficulty, as regards the physics of the question, can be raised against the idea that atmospheric carbon dioxide reaches the active centres of assimilation by a process of free diffusion through the leaf stomata.

One of the most interesting problems connected with plant assimilation relates to the efficiency of a green leaf as an absorber and transformer of the radiant energy incident upon it.

It is already well known that the actual amount of energy stored up in the products of assimilation bears a very small proportion to the total amount reaching the leaf: in other words, the leaf, regarded from a thermodynamic point of view, is a machine with a very low "economic coefficient." We require, however, to know much more than this, and to ascertain, amongst other things, how the efficiency of the machine varies under different conditions of insolation, and in atmospheres containing varying amounts of carbon dioxide.

The measure of the two principal forms of work done within the leaf, the vaporisation of the transpiration water on the one hand, and the reduction of carbon dioxide and water to the form of carbohydrates on the other, can be ascertained by modifying our experiments in such a manner as to allow the transpiration water to be determined, as well as the intake of carbon dioxide.

For the actual measurement of the total energy incident on the leaf under various conditions we are now using one of Professor Callendar's recording radiometers of specially delicate construction, which will be ultimately calibrated in calories. This instrument gives promise of excellent results, but up to the present time the work we have done with it is not sufficiently advanced for me to describe. We may, however, obtain a very fair idea of the variation in the efficiency of a leaf from one or two examples in which the amount of incident energy was deduced from other considerations.

In the case of a sunflower leaf exposed to the strong sunlight of a brilliant day in August the average amount of radiant energy falling on the leaf during the five hours

occupied by the experiment was estimated at 600,000 calories per square metre per hour. The average hourly transpiration of water during that time was at the rate of 275 c.c. per square metre, and the assimilated carbohydrate, estimated by the intake of carbon dioxide, was at the rate of 0·8 grm. per square metre per hour.

The vaporisation of 275 c.c. of water must have required the expenditure of 166,800 calories, and the endothermic production of 0·8 grm. of carbohydrate (taking the heat of combustion at 4000 grm. calories) corresponds to the absorption of 3200 calories. Thus, as the final result under these particular conditions of experiment, we find that the leaf has absorbed and converted into internal work about 28 per cent of the total radiant energy incident on it, 27·5 per cent being used up in the vaporisation of water, and only *one-half per cent* in the actual work of assimilation.

In strong diffuse light, such as that from a northern sky on a clear summer's day, the leaf has a higher "economic coefficient," using that term in relation to the permanent storage of energy in the assimilatory products. In one instance of this kind in which the total energy received by the leaf was approximately 60,000 calories per square metre per hour, it was found that 96 c.c. of water were evaporated and 0·41 grm. of carbohydrate was formed for the same area and time. This indicates an absorption and utilisation by the leaf of something like 95 per cent of the incident energy, of which 2·7 per cent has been made use of for actual work of assimilation as against 0·5 per cent in brilliant sunshine.*

From what I have said previously about the effect of increased tension of carbon dioxide on the rate of assimilation, it must follow that the "efficiency" of a leaf as regards the permanent storage of energy must, *cæteris paribus*, be increased when small additions of that gas are made to the surrounding air.

In one such instance, in which the air had been enriched with carbon dioxide to the extent of about five-and-a-half times the normal amount, it was estimated that the "efficiency" of the leaf for bright sunshine was raised from 0·5 to 2·0 per cent.

Up to the present we have been regarding the efficiency of the assimilatory mechanism of a plant in reference to the *total* energy of all grades which falls upon the leaf. It is of course well known that the power of decomposing carbon dioxide is limited to rays of a certain refrangibility, and the researches of Timiriazeff, Engelmann, and others leaves little room to doubt that the rays of the spectrum which are instrumental in producing the reaction in the chloroplastids have a distinct relation to the absorption-bands of the leaf-chlorophyll. By far the greater amount of the assimilatory work, probably more than 90 per cent of it, is effected by the rays which correspond to the principal absorption-band in the red, lying between wave-lengths 6500 and 6975.† If, therefore, we express the distribution of energy in a normal solar spectrum in the form of a curve, we have the means of approximately determining the *maximum theoretical efficiency* of a green leaf; that is to say, the maximum amount of assimilatory work which could be produced, supposing the conditions so favourable as to admit of the whole of the energy corresponding to this absorption-band being stored up within the leaf.

It is not without interest to get an approximate idea of this theoretical maximum.

For this purpose I have here reproduced a curve given by Professor S. P. Langley, representing the distribution of energy at the sea-level in the normal spectrum of a vertical sun shining in a clear sky (Fig. 3). The total amount of incident energy represented by the whole area of the curve is 1·7 calories per square centimetre per minute, or 1,020,000 calories per square metre per hour.

I have drawn a thick black vertical band in the red end of the spectrum corresponding in position and breadth with the principal absorption band of chlorophyll as seen in a green leaf. By integration it may be shown that the area of this part of the curve is about 6·5 per cent of that of the whole curve, so that this value represents something like the theoretical maximum efficiency of a leaf in bright vertical sunshine, supposing the conditions could be made so favourable as to result in a complete filtering-out and utilisation of the whole of the rays of the right period for producing decomposition of carbon dioxide.

This maximum efficiency expressed in calories per square metre per hour is 66,300, corresponding to the heat of formation of about 16·5 grms. of carbohydrate. Under the most favourable conditions we have employed up to the present we have not obtained a larger production than about 3·0 grms. of carbohydrate per square metre per hour, or about 18 per cent of the theoretical maximum; but this was in air containing only 16·4 parts of carbon dioxide per 10,000, which must be very far below the true optimum amount.

The brilliant discoveries of recent years on the constitution and synthesis of the carbohydrates have not brought us sensibly nearer to an explanation of the first processes of the reduction of carbon dioxide in the living plant. The hypothesis of Baeyer still occupies the position it did when it was first put forward nearly thirty years ago, although it has, it is true, received a certain amount of support from the observations of Bokorny, who found that formaldehyde can, under certain conditions, contribute to the building up of carbohydrates in the chloroplasts.

The changes which go on in the living cell are so rapid, and are of such a complex kind, that there seems little or no hope of ascertaining the nature of the first steps in the process unless we can artificially induce them under much simpler conditions.

The analogy which exists between the action of chlorophyll in the living plant and that of a *chromatic sensitiser* in a photographic plate, was, I believe, first pointed out by Captain Abney, and was more fully elaborated by Timiriazeff, who was inclined to regard chlorophyll as the sensitiser *par excellence*, since it absorbs and utilises for the assimilatory process the radiations corresponding approximately to the point of maximum energy in the normal spectrum. The view which Timiriazeff has put forward, that there is a mere physical transference of vibrations of the right period from the absorbing chlorophyll to the reacting carbon dioxide and water, is, I think, far too simple an explanation of the facts. Chromatic sensitisers have been shown to act by reason of their antecedent decomposition and not by direct transference of energy, and the same probably holds good with regard to chlorophyll, which is also decomposed by the rays which it absorbs. We must probably seek for the first and simplest stages of the assimilatory process in the interaction of the reduced constituents of the chlorophyll and the elements of carbon dioxide and water, the combinations so formed being again split up in another direction by access of energy from without.

* The principal factor which determines the amount of transpiration in a plant must be the amount of radiation falling on it. It is essential that the water-bearing mechanism should be able to keep up a good supply of water to the leaf lamina in order to prevent the temperature rising to a dangerously high point. This "safety valve" function of the transpiration current is not always sufficiently borne in mind, and we are too apt to think that the plant requires these enormous amounts of water in order to supply itself with the requisite mineral salts. The absolute necessity for the supply as a dissipator of energy will become evident by taking one or two facts into consideration. A square metre of the lamina of the leaf of a sunflower weighs about 250 grms., and its specific heat is about 0·9. We have seen that the hourly transpiration in bright sunshine may be as much as 275 c.c. per square metre, requiring the expenditure of 162,800 calories, and it therefore follows that, if the loss of water were stopped, the temperature of the leaf would rise at the rate of more than 12° C. *per minute*. In making our experiments in glazed cases it has sometimes been very interesting to watch the result of any accidental stoppage of the water-current in the leaf-stalk, and the almost instantaneous effect this has in destroying the leaf when the insolation is of high intensity.

† These limits are those of the band as measured by passing sunlight through the leaf itself. In an alcoholic solution of chlorophyll the band lies between λ 6400 and λ 6850. I must here express my thanks to Mr. Charles A. Schunck for having kindly undertaken to make these measurements for me.

The failure of all attempts to produce such a reaction under artificial conditions is, I think, to be accounted for by the neglect of one very important factor. We are dealing with a reaction of a highly endothermic nature, which is probably also highly *reversible*, and on this account we cannot expect any sensible accumulation of the products of change unless we employ some means for removing them from the sphere of action as fast as they are formed.

In the plant this removal is provided for by the living elements of the cell, by the chloroplast, assisted no doubt by the whole of the cytoplasm. We have here, in fact, the analogue of the *chemical sensitisers* of a photographic plate, which act as halogen absorbers and so permit a sensible accumulation of effect on the silver salts.

When we have succeeded in finding some simple chemical means of fixing the initial products of the reduction of carbon dioxide, then, and then only, may we hopefully look forward to reproducing in the laboratory the first stages of the great synthetic process of Nature on which the continuance of all life depends.

ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION.

DOVER, 1899.

By J. H. POYNTING, D.Sc., F.R.S.,
President of the Section.

THE members of this Section will, I am sure, desire me to give expression to the gratification that we all feel in the realisation of the scheme first proposed from this chair by Dr. Lodge, the scheme for the establishment of a National Physical Laboratory. It would be useless here to attempt to point out the importance of the step taken in the definite foundation of the Laboratory, for we all recognise that it was absolutely necessary for the due progress of physical research in this country. It is matter for congratulation that the initial guidance of the work of the Laboratory has been placed in such able hands.

While the investigation of Nature is ever increasing our knowledge, and while each new discovery is a positive addition never again to be lost, the range of the investigation and the nature of the knowledge gained form the theme of endless discussion. And in this discussion, so different are the views of different schools of thought, that it might appear hopeless to look for general agreement, or to attempt to mark progress.

Nevertheless, I believe that in some directions there has been real progress, and that physicists, at least, are tending towards a general agreement as to the nature of the laws in which they embody their discoveries, of the explanations which they seek to give, and of the hypotheses they make in their search for explanations.

I propose to ask you to consider the terms of this agreement, and the form in which, as it appears to me, they should be drawn up.

The range of the physicist's study consists in the visible motions and other sensible changes of matter. The experiences with which he deals are the impressions on his senses, and his aim is to describe in the shortest possible way how his various senses have been, will be, or would be affected.

His method consists in finding out all likenesses, in classing together all similar events, and so giving an account as concise as possible of the motions and changes observed. His success in the search for likenesses and his striving after conciseness of description lead him to imagine such a constitution of things that likenesses exist even where they elude his observation, and he is thus enabled to simplify his classification on the assumption that the constitution thus imagined is a reality. He is enabled to predict on the assumption that the likenesses of the future will be the likenesses of the past.

His account of Nature, then, is—as it is often termed—a descriptive account.

Were there no similarities in events, our account of them could not rise above a mere directory, with each individual event entered up separately with its address. But the similarities observed enable us to class large numbers of events together, to give general descriptions, and indeed to make, instead of a directory, a readable book of science, with laws as the headings of the chapters.

These laws are, I believe, in all cases brief descriptions of observed similarities. By way of illustration let us take two or three examples.

The law of gravitation states that to each portion of matter we can assign a constant—its mass—such that there is an acceleration towards it of other matter proportional to that mass divided by the square of its distance away. Or all bodies resemble each other in having this acceleration towards each other.

Hooke's law for the case of a stretched wire states that each successive equal small load produces an equal stretch, or states that the behaviour of the wire is similar for all equal small pulls.

Joule's law for the heat appearing when a current flows in a wire states that the rate of heat development is proportional to the square of the current multiplied by the resistance, or states that all the different cases resemble each other in having $H \div C^2Rt$ constant.

And, generally, when a law is expressed by an equation, that equation is a statement that two different sets of measurements are made, represented by the terms on the two sides of the equation, and that all the different cases resemble each other in that the two sets have the constant relation expressed by the equation. Accurate prediction is based on the assumption that when we have made the measurements on the one side of the equation we can tell the result of the measurements implied on the other side.

If this is a true account of the nature of physical laws, they have, we must confess, greatly fallen off in dignity. No long time ago they were quite commonly described as the Fixed Laws of Nature, and were supposed sufficient in themselves to govern the universe. Now we can only assign to them the humble rank of mere descriptions, often tentative, often erroneous, of similarities which we believe we have observed.

The old conception of laws as self-sufficing governors of Nature was, no doubt, a survival of a much older conception of the scope of physical science, a mode of regarding physical phenomena which had itself passed away.

I imagine that originally man looked on himself and the result of his action in the motions and changes which he produced in matter, as the one type in terms of which he should seek to describe all motions and changes. Knowing that his purpose and will were followed by motions and changes in the matter about him, he thought of similar purpose and will behind all the motions and changes which he observed, however they occurred; and he believed, too, that it was necessary to think thus in giving any consistent account of his observations. Taking this anthropomorphic—or, shall we say, psychical—view, the laws he formulated were not merely descriptions of similarities of behaviour, but they were also expressions of fixed purpose and the resulting constancy of action. They were commands given to matter which it must obey.

The psychical method, the introduction of purpose and will, is still appropriate when we are concerned with living beings. Indeed it is the only method which we attempt to follow when we are describing the motions of our fellow-creatures. No one seeks to describe the motions and actions of himself and of his fellow-men, and to classify them without any reference to the similarity of purpose when the actions are similar. But as the study

of Nature progressed, it was found to be quite futile to bring in the ideas of purpose and will when merely describing and classifying the motions and changes of non-living matter. Purpose and will could be entirely left out of sight, and yet the observed motions and changes could be described, and predictions could be made as to future motions and changes. Limiting the aim of physical science to such description and prediction, it gradually became clear that the method was adequate for the purpose, and over the range of non-living matter, at least, the psychical yielded to the physical. Laws ceased to be commands analogous to legal enactments, and became mere descriptions. But during the passage from one position to the other, by a confusion of thought which may appear strange to us now that we have finished the journey, though no doubt it was inevitable, the purpose and will of which the laws had been the expression were put into the laws themselves; they were personified and made to will and act.

Even now these early stages in the history of thought can be traced by survivals in our language, survivals due to the ascription of moral qualities to matter. Thus gases are still sometimes said to obey or to disobey Boyle's Law as if it were an enactment for their guidance, and as if it set forth an ideal, the perfect gas, for their imitation. We still hear language which seems to imply that real gases are wanting in perfection, in that they fail to observe the exact letter of the law. I suppose on this view we should have to say that hydrogen is nearest to perfection; but then we should have to regard it as righteous over-much, a sort of Pharisee among gases which overshoots the mark in its endeavour to obey the law. Oxygen and nitrogen we may regard as good enough in the affairs of everyday life. But carbon dioxide and chlorine and the like are poor sinners which yield to temptation and liquefy whenever circumstances press at all hardly on them.

There is a similar ascription of moral qualities when we judge bodies according to their fulfilment of the purpose for which we use them, when we describe them as good or bad radiators, good or bad insulators, as if it were a duty on their part to radiate well, or insulate well, and as if there were failures on the part of Nature to come up to the proper standard.

These are of course mere trivialities, but the reaction of language on thought is so subtle and far-reaching that, risking the accusation of pedantry, I would urge the abolition of all such picturesque terms. In our quantitative estimates let us be content with "high" or "low," "great" or "small," and let us remember that there is no such thing as a failure to obey a physical law. A broken law is merely a false description.

Concurrently with the change in our conception of physical law has come a change in our conception of physical explanation. We have not to go very far back to find such a statement as this, that we have explained anything when we know the cause of it, or when we have found out the reason why—a statement which is only appropriate on the psychical view. Without entering into any discussion of the meaning of cause, we can at least assert that that meaning will only have true content when it is concerned with purpose and will. On the purely physical or descriptive view, the idea of cause is quite out of place. In description we are solely concerned with the "how" of things, and their "why" we purposely leave out of account. We explain an event not when we know "why" it happened, but when we show "how" it is like something else happening elsewhere or otherwhen—when, in fact, we can include it as a case described by some law already set forth. In explanation, we do not account *for* the event, but we improve our account *of* it by likening it to what we already knew.

For instance, Newton explained the falling of a stone when he showed that its acceleration towards the earth was similar to and could be expressed by the same law as the acceleration of the moon towards the earth.

He explained the air disturbance we call "sound" when he showed that the motions and forces in the pressure waves were like motions and forces already studied.

Franklin explained lightning when and so far as he showed that it was similar in its behaviour to other electric discharges.

Here I do not fear any accusation of pedantry in joining those who urge that we should adapt our language to the modern view. It would be a very real gain, a great assistance to clear thinking, if we could entirely abolish the word "cause" in physical description, cease to say "why" things happen unless we wish to signify an antecedent purpose, and be content to own that our laws are but expressions of "how" they occur.

The aim of explanation, then, is to reduce the number of laws as far as possible, by showing that laws, at first separated, may be merged in one; to reduce the number of chapters in the book of science by showing that some are truly mere sub-sections of chapters already written.

To take an old but never worn-out metaphor, the physicist is examining the garment of Nature, learning of how many, or rather of how few, different kinds of thread it is woven, finding how each separate thread enters into the pattern, and seeking from the pattern woven in the past to know the pattern yet to come.

How many different kinds of thread does Nature use?

So far, we have recognised some eight or nine, the number of different forms of energy which we are still obliged to count as distinct. But this distinction we cannot believe to be real. The relations between the different forms of energy, and the fixed rate of exchange when one form gives place to another, encourage us to suppose that if we could only sharpen our senses, or change our point of view, we could effect a still further reduction. We stand in front of Nature's loom as we watch the weaving of the garment; while we follow a particular thread in the pattern it suddenly disappears, and a thread of another colour takes its place. Is this a new thread, or is it merely the old thread turned round and presenting a new face to us? We can do little more than guess. We cannot get to the other side of the pattern, and our minutest watching will not tell us all the working of the loom.

Leaving the metaphor, were we true physicists, and physicists alone, we should, I suppose, be content to describe merely what we observe in the changes of energy. We should say, for instance, that so much kinetic energy ceases, and that so much heat appears, or that so much light comes to a surface, and that so much chemical energy takes its place. But we have to take ourselves as we are, and reckon with the fact that though our material is physical, we ourselves are psychical. And, as a mere matter of fact, we are not content with such discontinuous descriptions. We dislike the discontinuity and we think of an underlying identity. We think of the heat as being that which a moment before was energy of visible motion, we think of the light as changing its form alone and becoming itself the chemical energy. Then to our passive dislike of discontinuity we join our active desire to form a mental picture of what may be going on, a picture like something which we already know. Coming on these discontinuities our ordinary method of explanation fails, for they are not obviously like those series of events in which we can trace every step. We then imagine a constitution of matter and modifications of it corresponding to the different kinds of energy, such that the discontinuities vanish, and such that we can picture one form of energy passing into another and yet keeping the same in kind throughout. We are no longer content to describe what we actually see or feel, but we describe what we imagine we should see or feel if our senses were on quite another scale of magnitude and sensibility. We cease to be physicists of the real and become physicists of the ideal.

To form such mental pictures we naturally choose the sense which makes such pictures most definite, the sense of sight, and think of a constitution of matter which

shall enable us to explain all the various changes in terms of visible motions and accelerations. We imagine a mechanical constitution of the universe.

We are encouraged in this attempt by the fact that the relations in this mechanical conception can be so exactly stated, that the equations of motion are so very definite. We have, too, examples of mechanical systems, of which we can give accounts far exceeding in accuracy the accounts of other physical systems. Compare, for instance, the accuracy with which we can describe and foretell the path of a planet with our ignorance of the movements of the atmosphere as dependent on the heat of the sun. The planet keeps to the astronomer's time-table, but the wind still bloweth almost where it listeth.

The only foundation which has yet been imagined for this mechanical explanation—if we may use "explanation" to denote the likening of our imaginings to that which we actually observe—is the atomic and molecular hypothesis of matter. This hypothesis arose so early in the history of science that we are almost tempted to suppose that it is a necessity of thought, and that it has a warrant of some higher order than any other hypothesis which could be imagined. But I suspect that if we could trace its early development we should find that it arose in an attempt to explain the phenomena of expansion and contraction, evaporation and solution. Were matter a continuum we should have to admit all these as simple facts, inexplicable in that they are like nothing else. But imagine matter to consist of a crowd of separate particles with interspaces. Contraction and expansion are then merely a drawing in and a widening out of the crowd. Solution is merely the mingling of two crowds, and evaporation merely a dispersal from the outskirts. The most evident properties of matter are then similar to what may be observed in any public meeting.

For ages the molecular hypothesis hardly went further than this. The first step onward was the ascription of vibratory motion to the atoms to explain heat. Then definite qualities were ascribed, definite mutual forces were called into play to explain elasticity and other properties or qualities of matter. But I imagine its first really great achievement was its success in explaining the law of combining proportions, and next to that we should put its success in explaining many of the properties of gases.

While light was regarded as corpuscular—in fact molecular, and while direct action at a distance presented no difficulty, the molecular hypothesis served as the one foundation for the mechanical representation of phenomena. But when it was shown that infinitely the best account of the phenomena of light could be given on the supposition that it consisted of waves, something was needed, as Lord Salisbury has said, to wave, both in the interstellar and in the intermolecular spaces. So the hypothesis of an ether was developed, a necessary complement of that form of the molecular hypothesis in which matter consists of discrete particles with matter-free intervening spaces.

Then Faraday's discovery of the influence of the dielectric medium in electric actions led to the general abandonment of the idea of action at a distance, and the ether was called in to aid matter in the explanation of electric and magnetic phenomena. The discovery that the velocity of electro-magnetic waves is the same as that of light waves is at least circumstantial evidence that the same medium transmits both.

I suppose we all hope that some time we shall succeed in attributing to this medium such further qualities that it will be able to enlarge its scope and take in the work of gravitation.

The mechanical hypothesis has not always taken this dualistic form of material atoms and molecules, floating in a quite distinct ether. I think we may regard Boscovich's theory of point-centres surrounded by infinitely extending atmospheres of force as really an attempt to get rid of the dualism, and Faraday's theory of point-centres with radiating lines of force is only Boscovich's theory in another form. But Lord Kelvin's vortex-atom theory gives us a simplification more easily thought of. Here all space is filled with continuous fluid—shall we say a fluid ether?—and the atoms are mere loci of a particular type of motion of this frictionless fluid. The sole differences in the atoms are differences of position and motion. Where there are whirls, we call the fluid matter; where there are no whirls, we call it ether. All energy is energy of motion. Our visible kinetic energy, $MV^2/2$, is energy in and round the central whirls; our visible energy of position, our potential energy, is energy of motion in the outlying regions.

A similar simplification is given by Dr. Larmor's hypothesis, in which, again, all space is filled with continuous substance all of one kind, but this time solid rather than fluid. The atoms are loci of strain instead of whirls, and the ether is that which is strained.

So, as we watch the weaving of the garment of Nature, we resolve it in imagination into threads of ether spangled over with beads of matter. We look still closer, and the beads of matter vanish; they are mere knots and loops in the threads of ether.

The question now faces us—How are we to regard these hypotheses as to the constitution of matter and the connecting ether? How are we to look upon the explanations they afford? Are we to put atoms and ether on an equal footing with the phenomena observed by our senses, as truths to be investigated for their own sake? Or are they mere tools in the search for truth, liable to be worn out or superseded?

That matter is grained in structure is hardly more than the expression of the fact that in very thin layers it ceases to behave as in thicker layers. But when we pass on from this general statement and give definite form to the granules or assume definite qualities to the intergranular cement, we are dealing with pure hypotheses.

It is hardly possible to think that we shall ever see an atom or handle the ether. We make no attempt whatever to render them evident to the senses. We connect observed conditions and changes in gross visible matter by invisible molecular and ethereal machinery. The changes at each end of the machinery of which we seek to give an account are in gross matter, and this gross matter is our only instrument of detection, and we never receive direct sense impressions of the imagined atoms or the intervening ether. To a strictly descriptive physicist their only use and interest would lie in their service in prediction of the changes which are to take place in gross matter.

It appears quite possible that various types of machinery might be devised to produce the known effects. The type we have adopted is undergoing constant minor changes, as new discoveries suggest new arrangements of the parts. Is it utterly beyond possibility that the type itself should change?

The special molecular and ethereal machinery which we have designed, and which we now generally use, has been designed because our most highly developed sense is our sense of sight. Were we otherwise, had we a sense more delicate than sight, one affording us material for more definite mental presentation, we might quite possibly have constructed very different hypotheses. Though, as we are, we cannot conceive any higher type than that founded on the sense of sight, we can imagine a lower type, and by way of illustration of the point let us take the sense of which my predecessor spoke last year—the sense of smell. In us it is very undeveloped. But let us imagine a being in whom it is highly cultivated, say, a very intellectual and very hypothetical dog. Let us suppose that he tries to frame an hypothesis as to light. Having found that his sense of smell is excited by surface exhalations, will he not naturally make and be content with a corpuscular theory of light? When he has discovered the facts of dispersion, will he not think of the different colours as different kinds of smell—in-

sensible, perhaps, to him, but sensible to a still more highly gifted, still more hypothetical dog?

Of course, with our superior intellect and sensibility, we can see where his hypothesis would break down; but unless we are to assume that we have reached finality in sense development, the illustration, grotesque as it may be, will serve to show that our hypotheses are in terms of ourselves rather than in terms of Nature itself, they are ejective rather than objective, and so they are to be regarded as instruments, tools, apparatus only to aid us in the search for truth.

To use an old analogy—and here we can hardly go except upon analogy—while the building of Nature is growing spontaneously from within, the model of it, which we seek to construct in our descriptive science, can only be constructed by means of scaffolding from without, a scaffolding of hypotheses. While in the real building all is continuous, in our model there are detached parts which must be connected with the rest by temporary ladders and passages, or which must be supported till we can see how to fill in the understructure. To give the hypotheses equal validity with facts is to confuse the temporary scaffolding with the building itself.

But even if we take this view of the temporary nature of our molecular and ethereal imaginings, it does not lessen their value, their necessity to us.

It is merely a true description of ourselves to say that we must believe in the continuity of physical processes, and that we must attempt to form mental pictures of those processes the details of which elude our observation. For such pictures we must frame hypotheses, and we have to use the best material at command in framing them. At present there is only one fundamental hypothesis—the molecular and ethereal hypothesis—in some such form as is generally accepted.

Even if we take the position that the form of the hypothesis may change as our knowledge extends, that we may be able to devise new machinery—nay, even that we may be able to design some quite new type to bring about the same ends—that does not appear to me to lessen the present value of the hypothesis. We can recognise to the full how well it enables us to group together large masses of facts which, without it, would be scattered apart, how it serves to give working explanations, and continually enables investigators to think out new questions for research. We can recognise that it is the symbolical form in which much actual knowledge is cast. We might almost as well quarrel with the use of the letters of the alphabet, inasmuch as they are not the sounds themselves, but mere arbitrary symbols of the sounds.

In this country there is no need for any defence of the use of the molecular hypothesis. But abroad the movement from the position in which hypothesis is confounded with observed truth has carried many through the position of equilibrium equally far on the other side, and a party has been formed which totally abstains from molecules as a protest against immoderate indulgence in their use. Time will show whether these protesters can do without any hypothesis, whether they can build without scaffolding or ladders. I fear that it is only an attempt to build from balloons.

But the protest will have value if it will put us on our guard against using molecules and the ether everywhere and everywhen. There is, I think, some danger, that we may get so accustomed to picturing everything in terms of these hypotheses that we may come to suppose that we have no firm basis for the facts of observation until we have given a molecular account of them, that a molecular basis is a firmer foundation than direct experience.

Let me illustrate this kind of danger. The phenomena of capillarity can, for the most part, be explained on the assumption of a liquid surface tension. But if the subject is treated merely from this point of view it stands alone—it is a portion of the building of science hanging in the air. The molecular hypothesis then comes in to give some explanation of the surface tension, gives, as it were, a supporting understructure connecting capillarity with other classes of phenomena. But here, I think, the hypothesis should stop, and such phenomena as can be explained by the surface tension should be so explained without reference to molecules. They should not be brought in again till the surface-tension explanation fails. It is necessary to bear in mind what part is scaffolding, and what is the building itself, already firm and complete.

Or, as another illustration, take the Second Law of Thermodynamics. I suspect that it is sometimes supposed that a molecular theory from which the Second Law could be deduced would be a better basis for it than the direct experience on which it was founded by Clausius and Kelvin, or that the mere imagining of a Maxwell's sorting demon has already disproved the universality of the law; whereas he is a mere hypothesis grafted on a hypothesis, and nothing corresponding to his action has yet been found.

There is more serious danger of confusion of hypothesis with fact in the use of the ether; more risk of failure to see what is accomplished by its aid. In giving an account of light, for instance, the right course, it appears to me, is to describe the phenomena and lay down the laws under which they are grouped, leaving it an open question what it is that waves, until the phenomena oblige us to introduce something more than matter, until we see what properties we must assign to the ether, properties not possessed by matter, in order that it may be competent to afford the explanations we seek. We should then realise more clearly that it is the constitution of matter which we have imagined, the hypothesis of discrete particles, which obliges us to assume an intervening medium to carry on the disturbance from particle to particle. But the vortex-atom hypothesis and Dr. Larmor's strain-atom hypothesis both seem to indicate that we are moving in the direction of the abolition of the distinction between matter and ether, that we shall come to regard the luminiferous medium not as an attenuated substance here and there encumbered with detached blocks,—the molecules of matter,—but as something which in certain places exhibits modifications which we term matter. Or starting rather from matter, we may come to think of matter as no longer consisting of separated granules, but as a continuum with properties grouped round the centres, which we regard as atoms or molecules.

Perhaps I may illustrate the danger in the use of the conception of the ether by considering the common way of describing the electro-magnetic waves, which are all about us here, as ether waves. Now in all cases with which we are acquainted, these waves start from matter; their energy before starting was, as far as we can guess, energy of the matter between the different parts of the source, and they manifest themselves in the receiver as energy of matter. As they travel through the air, I believe that it is quite possible that the electric energy can be expressed in terms of the molecules of air in their path, that they are effecting atomic separations as they go. If so, then the air is quite as much concerned in their propagation as the ether between its molecules. In any case, to term them ether waves is to prejudge the question before we have sufficient evidence.

Unless we bear in mind the hypothetical character of our mechanical conception of things, we may run some risk of another danger—the danger of supposing that we have something more real in mechanical than in other measurements. For instance, there is some risk that the work measure of specific heat should be regarded as more fundamental than the heat measure, in that heat is truly a "mode of motion." On the molecular hypothesis, heat is no doubt a mixture of kinetic energy and potential energy of the molecules and their constituents, and may even be entirely kinetic energy; and we may conceivably in the future make the hypothesis so definite that, when we heat a grm. of water 1°, we can assign such a fraction of an erg to each atom. But look how much pure hypothesis is here. The real superiority of the work measure

of specific heat lies in the fact that it is independent of any particular substance, and there is nothing whatever hypothetical about it.*

Another illustration of the illegitimate use of our hypothesis, as it appears to me, is in the attempt to find in the ether a fixed datum for the measurement of material velocities and accelerations, a something in which we can draw our co-ordinate axes so that they will never turn or bend. But this is as if, discontented with the movement of the earth's pole, we should seek to find our zero lines of latitude and longitude in the Atlantic Ocean. Leaving out of sight the possibility of ethereal currents which we cannot detect, and the motions due to every ray of light which traverses space, we could only fix positions and directions in the ether by buoying them with matter. We know nothing of the ether, except by its effects on matter, and, after all, it would be the material buoys which would fix the positions and not the ether in which they float.

The discussion of the physical method, with its descriptive laws and explanations, and its hypothetical extension of description, leads us on to the consideration of the limitation of its range. The method was developed in the study of matter which we describe as non-living, and with non-living matter the method has sufficed for the particular purposes of the physicist. Of course only a little corner of the universe has been explored, but in the study of non-living matter we have come to no impassable gulfs, no chasms across which we cannot throw bridges of hypothesis. Does the method equally suffice when it is applied to living matter? Can we give a purely physical account of such matter, likening its motions and changes to other motions and changes already observed, and so explaining them? Can we group them in laws which will enable us to predict future conditions and positions? The ancient question never answered, but never ceasing to press for an answer.

Having faith in our descriptive method, let us use it to describe our real attitude on the question. Do we, or do we not, as a matter of fact, make any attempt to apply the physical method to describe and explain those motions of matter which on the psychical view we term voluntary?

Any commonplace example—and the more commonplace the more is it to the point—will at once tell us our practice, whatever may be our theory. For instance, a steamer is going across the Channel. We can give a fairly good physical account of the motion of the steamer. We can describe how the energy stored in the coal passes out through the boiler into the machinery, and how it is ultimately absorbed by the sea. And the machinery once started, we can give an account of the actions and reactions between its various parts and the water, and, if only the crew will not interfere, we can predict with some approach to correctness how the vessel will run. All these processes can be likened to processes already studied—perhaps on another scale—in our laboratories, and from the similarities prediction is possible. But now think of a passenger on board who has received an invitation to take the journey. It is simply a matter of fact that we make no attempt at a complete physical account and explanation of those actions which he takes to accomplish his purpose. We trace no lines of induction in the ether connecting him with his friends across the Channel, we seek no law of force under which he moves. In practice the strictest physicist abandons the physical view, and replaces it by the psychical. He admits the study of purpose as well as the study of motion.

He has to admit that here his physical method of prediction fails. In physical observations one set of measurements may lead to the prediction of the results of another set of measurements. The equations expressing the laws imply different observations with some definite relation between their results, and if we know one set of observations and that definite relation we can predict the result of the other set. But if we take the psychical view of actions we can only measure the actions. We have no independent means of studying and measuring the motions which preceded the actions, we can only estimate their value by the consequent actions. If we formed equations, they would be mere identities with the same terms on either side.

The consistent and persistent physicist, finding the door closed against him, finding that he has hardly a sphere of influence left to him in the psychical region, seeks to apply his methods in another way by assuming that if he knew all about the molecular positions and motions in the living matter, then the ordinary physical laws could be applied and the physical conditions at any future time could be predicted. He would say, I suppose, with regard to the Channel passenger, that it is absurd to begin with the most complicated mechanism, and seek to give a physical account of that. He would urge that we should take some lower form of life where the structure and motions are simpler, and apply the physical methods to that.

Well, then, let us look for the physical explanation of any motion which we are entitled from its likeness to our own action to call a voluntary motion. Must we not own that even the very beginning of such explanation is as yet non-existent? It appears to me that the assumption that our methods do apply, and that purely physical explanation will suffice to predict all motions and changes, voluntary and involuntary, is at present simply a gigantic extra-polation, which we should unhesitatingly reject if it were merely a case of ordinary physical investigation. The physicist when thus extending his range is ceasing to be a physicist, ceasing to be content with his descriptive methods in his intense desire to show that he is a physicist throughout.

Of course we may describe the motions and changes of any type of matter after the event, and in a purely physical manner. And as Professor Ward has suggested, in a most important contribution to this subject which he has made in his recently published "Gifford Lectures" ('Naturalism and Agnosticism,' "The Gifford Lectures," 1896-98, vol. ii., p. 71), where ordinary physical explanations fail to give an account of the motions, we might imagine some structure in the ether, and such stresses between the ether and matter that our physical explanations should still hold. But, as Professor Ward says, such ethereal constructions would present no warrant for their reality or consistency. Indeed they would be mere images in the surface of things to account for what goes on in front of the surface, and would have no more reality than the images of objects in a glass.

If we have full confidence in the descriptive method, as applied to living and non-living matter, it appears to me that up to the present it teaches us that while in non-living matter we can always find similarities, that, while each event is like other events, actual or imagined, in a living being there are always dissimilarities. Taking the psychical view—the only view which we really do at present take—in the living being there is always some individuality, something different from any other living being, and full prediction in the physical sense, and by physical methods is impossible. If this be true, the loom of Nature is weaving a pattern with no mere geometrical design. The threads of life, coming in we know not

* This risk of imagining one particular kind of measure more real than another, more in accordance with the truth of things, may be further illustrated by the common idea that mass-acceleration is the only way to measure a force. We stand apart from our mechanical system and watch the motions and the accelerations of the various parts, and we find that mass-accelerations have a certain significance in our system. If we keep ourselves outside the system and only use our sense of sight, then mass-acceleration is the only way of describing that behaviour of one body in the presence of others which we term force on it. But if we go about in the system and pull and push bodies, we find that there is another conception of force, in which another sense than sight is concerned,—another mode of measurement much more ancient and still far more extensively used, the measurement by weight supported. Each method has its own range; each is fundamental in that range. It is one of the great practical problems in physics to make the pendulum give us the exact ratio of the units in the two systems.

where, now twining together, now dividing, are weaving patterns of their own, ever increasing in intricacy, ever gaining in beauty.

CORRESPONDENCE.

THE MELTING-POINT OF HYDROGEN.

To the Editor of the Chemical News.

SIR,—The value, about 16·7° C. (abs.), is given by Prof. Dewar for the melting-point of hydrogen in his recent important communication to the British Association, as reported in the CHEM. NEWS, vol. lxxx., p. 132.

A simple calculation shows that a value near to this, viz., 16·768° C. (abs.) is, within narrow limits, a common measure of the melting-points of the family of alkali-metals of which hydrogen is the first member. Thus, taking the determinations given in Roscoe and Schorlemmer's "Chemistry," latest edition, p. 56—

	M.P. (abs.).	16·768		Diff.
H	c. 16·7 (Dewar)	X		
Li	453	27	= 452·73	−0·27
Na	368·6	22	= 368 89	−0·29
K	335·5	20	= 335·36	−0·14
Rb	311·5	18·5	= 310·20	−1·3
Cs	299·5	18	= 301·82	+1·3
—	c. 273	17·5	= 293·44	

c. 293 is the melting-point for the unknown alkali-metal (A W c. 223·7) next succeeding to Cs, independently arrived at by a graphical treatment of the melting-points of the elements in a manner similar to that employed for the A.V.'s (*Journ. Am. Chem. Soc.*, xx., No. 12). This graphical treatment clearly demonstrates an interrelation between the A.V.'s, M.P.'s, and B.P.'s of the elements, and in view of the figures given above the question may be asked whether the melting-points of the alkali-metals are not simple multiples of the melting-point of hydrogen. Also, taking 0·086 (Dewar) as the maximum density of liquid hydrogen (= A.V. 11·6), the A.V.'s of the same metals are (but only approximately) simple multiples of this hydrogen value.—I am, &c.,

THOMAS BAYLEY.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 9, August 28, 1899.

Velocity of Detonation of Acetylene.—MM. Berthelot and Le Chatelier.—The authors have studied the velocity of propagation of the detonation of acetylene under different pressures and with other varying conditions. This investigation is interesting, both from the point of view of the theory of propagation of physico-chemical reactions in gases, and also from the point of view of the rules of employment of this gas for illuminating purposes. The gas was contained in horizontal glass tubes about 1 metre long and of diameter between 2 and 6 m.m. It was introduced under pressures varying between 5 and 36 atmospheres, and was found to contain 98 per cent of acetylene. The gas was fired electrically, a small piece of fulminate being used, and the registration of the phenomena was made by the photographic method, which method gives an exact record of all the phases—at least, in so far as the gas remains luminous.

No. 10, September 4, 1899.

This issue contains no chemical matter.

MISCELLANEOUS

Merchant Venturers' Technical College, Bristol.—*Chemistry and Metallurgy.*—Principal, Professor Julius Wertheimer, B.Sc., F.C.S., &c., assisted by Messrs. G. P. Darnell-Smith, B.Sc., &c., H. A. M. Borland, A.R.C.S., H. R. Tutton, F. B. Gatehouse, and W. H. Collier. Physics: Professor A. Philip, B.Sc., and W. G. Hibbins, A.I.E.E., assisted by Messrs. H. E. U. Roberts, W. F. Gibson, and James H. Brinkworth. The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to students of either sex. They include the Junior Laboratory (for 40 students working at one time), Senior Laboratory, Gas Analysis Room, Balance Room, Combustion Room, Store Rooms, and Metallurgical Laboratory. The training in this department is intended to fit students to become professional chemists, to prepare them for medical or pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying. Special facilities will be given to students wishing to undertake research work approved by the Principal; and the courses provide completely for the Preliminary Scientific Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. degree of the University of London. The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute, provided the details in each case be certified by the Professors. Certificates of Proficiency in Assaying will be given to students who complete a course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College Examinations in the Theory and Practice of Assaying. The annual fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop. Twelve of the students of the College were successful at the last Intermediate B.Sc. Examination of the University of London, and one obtained First Class Honours and two Second Class Honours in Chemistry. The College Evening Classes, available to persons of either sex, will commence on Monday, October 2nd.

On the Chlorinised, Bromised, and Nitrated Derivatives of the Phenetidines, as well as on some Azoïc Colouring-matters derived from them.—F. Rierdin and F. Düring.—The authors have endeavoured to decide what is the influence of the respective groups NH_2, NO_2, and also the group NH_2 and Cl or Br on the shade of the azoïc colouring-matters obtained with the chlorinised, brominised, and nitrated derivatives of the phenetidines. With this object they prepared a number of derivatives, the full description of the preparation and properties of which, as well as a description of their derivatives and the determination of their constitutions, will be found in the *Archives des Science Physiques et Naturelles*, vol. vii., No. 4, p. 201. These bases were utilised either for the production of colouring-matters for fibre treated with β-naphthol, or for the preparation of certain azoïc colours; in particular, those derived from salicylic acid, from 1:4-naphtholsulphonic acid of the salt R, from G-amidonaphtholsulphonic acid, and from chromotrope. The result of the experiments shows that, with the chlorised and bromised derivatives, the derivative $C_6H_3.OC_2H_5.NH_2.NO_2$ 1:2:4 gives a much deeper tint than the corresponding derivatives containing Cl or Br in the place of NO_2.—*Bulletin de la Soc. Chim. de Paris*, Series 3, vol. xxi., No. 7.

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DAVID LEWIS, Treasurer.
Treasurer's Chambers, 20, York Place,
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THE CHEMICAL NEWS.

Vol. LXXX., No. 2080.

NOTE ON THE ACTION OF LIGHT UPON METALLIC SILVER.*

By Major-General J. WATERHOUSE,
Hon. Sec. of the Royal Photographic Society.

Following on the lines of Moser's thermographic observations, it may be asserted that metallic silver is sensitive to light. If cut-out masks be laid upon the surface of silver leaf or foil, silvered glass, or on a Daguèrreotype plate and exposed to the sun's rays a visible image ultimately becomes apparent on the metallic surface. The effect may, however, be got in a very much shorter space of time if the partly exposed metal be subjected to mercury vapour, or developed by immersion in an acid solution of a ferrous salt mixed with nitrate of silver. Clear images, hardly as yet to be called pictures, can thus be obtained of a permanent character, so that it may be possible to work the Daguèrreotype process without iodising the plate. In fact, the photographic phenomena of the invisible developable image, the visible image, reversal, and the effect of pressure marks can all be illustrated on the plain silver surface.

This at least is a new discovery.

Copper seems to be sensitive in the same way, and doubtless other metals.

Postscript.—To avoid contact, a thin sheet of mica was interposed between the silver plate and mask in most of the experiments without appreciably affecting the result.

ON THE PERMANENCE OF CERTAIN GASES IN THE ATMOSPHERES OF PLANETS.†

By G. H. BRYAN, Sc.D., F.R.S.

In a paper read before the Nottingham Meeting of the Association, the author discussed the application of the kinetic theory of gases to explain the absence of an atmosphere from the moon's surface. In the present investigation similar methods are applied to the atmospheres of planets, account being taken of the axial rotations of the planets. A test of the permanence or otherwise of different gases in the atmospheres of different celestial bodies at different temperatures has been obtained, and a superior limit has been found for the rate at which any planet would lose any gas by the molecules flying off from its atmosphere. To interpret this limit in the simplest possible form, the author has calculated the number of years which would have to elapse in various cases before the quantity of gas lost would be equivalent to that contained in a layer one centimetre thick, covering the surface of the earth. For simplicity absolute temperatures of 200°, 300°, 400°, 500°, and 600° have been chosen—*i.e.*, Centigrade temperatures of −73°, 27°, 127°, and so forth.

In the case of terrestrial hydrogen the loss in question would occupy 84,000,000,000 years at temperature −73°, 600,000 years at −23°, and 222 years at 27° C.

For helium on the earth's surface, the corresponding numbers are $3{\cdot}5\times10^{36}$ years at −73°, 3×10^{19} or 30 trillion years at 27°, 84,000,000,000 years at 127°, 600,000 years at 227°, and 222 years at 327°.

For vapour of water on Mars, the figures are $1{\cdot}2\times10^{33}$ years at −73°, $1{\cdot}9\times10^{16}$, or 19 thousand billion years at 27°, 2,400,000,000 years at 127°, 43,000 years at 227°, and 106 years at 327°.

The removal of a layer of *air* 1 c.m. in thickness from the surface of the earth would only mean a lowering in the average barometric pressure of $\frac{1}{13600}$ of a m.m., roughly. Suppose then that the afore-mentioned gases were present in the respective atmospheres in sufficient quantity to produce pressures comparable with one atmosphere, and assume that a fall of 1 m.m. in the average height of the barometer is the least secular change that could be detected; the above-mentioned intervals of time would have to be multiplied by 13,600 roughly, in order to give the numbers of years in which the escape of the respective gases could be detected by a barometer.

The only possible conclusions from these results are—

1. That helium could exist permanently in our atmosphere at ordinary temperatures.
2. That watery vapour could exist permanently in the atmosphere of Mars at ordinary temperatures.
3. That if helium once existed in appreciable quantities in the earth's atmosphere, it must have escaped when the earth was far hotter than at present.
4. That a similar conclusion holds good on the supposition that Mars once possessed, but has now lost, vapour of water as a constituent of its atmosphere, the temperature-limit at which the loss ceased to be appreciable being, however, lower than for terrestrial helium.
5. That hydrogen, on the other hand, may escape to an appreciable extent from the earth's atmosphere even at ordinary temperatures.

In Dr. Johnstone Stoney's paper it was assumed that helium would escape from the earth's atmosphere, and the author deduced that water could not exist on Mars. Dr. Stoney assumed a temperature of −66° C. in his investigations. It will be seen that the present conclusions for such low temperatures are contrary to Dr. Stoney's hypothesis.

WATER AND SEWAGE EXAMINATION RESULTS.*

Report of the Committee appointed to establish a Uniform System of recording the Results of the Chemical and Bacterial Examination of Water and Sewage.

The Committee beg to report as follows;—That it is desirable that results of analysis should be expressed in parts per 100,000, except in the case of dissolved gases, when these should be stated as cubic centimetres of gas at 0° C. and 760 m.m. in 1 litre of water. This method of recording results is in accordance with that suggested by the Committee appointed in 1887 to confer with the Committee of the American Association for the Advancement of Science with a view to forming a uniform system of recording the results of water analysis (*Brit. Assoc. Report*, 1889).

2. The Committee suggest that in the case of all nitrogen compounds the results be expressed as parts of nitrogen over 100,000, including the ammonia expelled on boiling with alkaline permanganate, which should be termed albumenoid nitrogen. The nitrogen will therefore be returned as—

1. Ammoniacal nitrogen from free and saline ammonia.
2. Nitrous nitrogen from nitrites.
3. Nitric nitrogen from nitrates.
4. Organic nitrogen (either by Kjeldahl or by combustion, but the process used should be stated).
5. Albumenoid nitrogen.

* Read before the British Association (Section B), Dover Meeting, 1899

† Read before the British Association (Section A), Dover Meeting, 1899.

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The total nitrogen of all kinds will be the sum of the first four determinations.

The Committee are of opinion that the percentage of nitrogen oxidised—that is, the ratio of 2 and 3 to 1 and 4—gives sometimes a useful measure of the stage of purification of a particular sample. The purification effected by a process will be measured by the amount of oxidised nitrogen as compared with the total amount of nitrogen existing in the crude sewage.

In raw sewage and in effluents containing suspended matter it is also desirable to determine how much of the organic nitrogen is present in the suspended matter.

In sampling, the Committee suggest that the bottles should be filled nearly completely with the liquid, only a small air-bubble being allowed to remain in the neck of the bottle. The time at which a sample is drawn, as well as the time at which its analysis is begun, should be noted. An effluent should be drawn to correspond as nearly as possible with the original sewage, and both it and the sewage should be taken in quantities proportional to the rate of flow when that varies (*e.g.*, in the emptying of a filter-bed).

In order to avoid the multiplication of analyses the attendant at a sewage works (or any other person who draws the samples) might be provided with sets of twelve or twenty-four stoppered ¼ Winchester bottles, one of which should be filled every hour or every two hours, and on the label of each bottle the rate of flow at the time should be written. When the bottles reach the laboratory quantities would be taken from each proportional to these rates of flow and mixed together, by which means a fair average sample for the twenty-four hours would be obtained.

The Committee at present are unable to suggest a method of reporting bacterial results, including incubator tests, which is likely to be acceptable to all workers.

THE TEACHING OF SCIENCE IN ELEMENTARY SCHOOLS.*

The progress in the teaching of science in elementary schools which was noted in the last report of your Committee has been more than maintained in so far as the number of scholars receiving instruction is concerned. Table A, made up from the return issued by the Education Department, gives the figures for the scientific class subjects, and for English by way of comparison. It will be remembered that for the eight years preceding the Code of 1890, English was obligatory as a class subject if any such subject was taken in the school. The placing it merely on a level with the other subjects had the effect of reducing the number of departments in which English was taken from 20,304 in 1889-90 to 19,825 in 1890-91, while in the same years the number of departments taking Elementary Science rose from the almost nominal figure of 32 to 173. The table shows the progress from that time onwards. It will be observed that there is an extraordinary increase in Object Lessons, which it was pointed out last year would be the case owing to the giving of Object Lessons in the three lower standards being made obligatory after September 1, 1896. The full effect of this change has hardly yet appeared. The return for 1897-98 should show a figure almost equal to the total number of departments. This ascendency of Object Lessons is fully capable of explaining the decrease in Elementary Science, and does not necessarily involve any lessening of the child's knowledge of Nature. It is rather a question of nomenclature than anything else, in some schools the object lessons course in the lower standards being still registered under the name of Elementary Science.

The number of departments in "schools for older scholars" for the year 1897-98 was 23,043, all but two of which took one or more class subjects. But History was taken in 5780 departments, and needlework (as a class subject for girls) in 7252 departments, and sundry minor subjects in 972, making, with the other four subjects of the table, a total of 68,534. This shows an average of very nearly three class subjects to each department, but it must be borne in mind that the same subject is not always taken in all the standards, in which case three or more class subjects will appear in the return for a single department.

It has been previously remarked that "the increased teaching of scientific specific subjects in the higher standards is the natural consequence of the greater attention paid to natural science in the lower part of the schools." Table B shows that such is the actual result. It may be noted that every one of these specific subjects shows an actual increase; and the totals indicate an increase of more than 20,000, a larger rise than has been recorded in any previous year.

In last year's report the number of scholars in Standards V., VI., and VII. was estimated at 615,000. The Government returns, in the form in which they are now presented, enable your Committee to make a much more precise estimate; and it now appears that the number of scholars, including the Ex-VII., must have been about 650,000. This figure would give 25·3 per cent as the proportion examined in these specific subjects as compared with the number of children qualified to take them, and the table below has been altered accordingly. The mean number of such scholars for the year 1897-98 is 693,242, which will give 26·6 per cent as the proportion of actual to possible students; but it should be remembered that many of the children take more than one subject for examination.

The following table gives the percentage for each year since 1882, and shows that the great depression which characterised several years has been succeeded by a gradual and steady rise:—

1882-83 ..	29·0 per cent		1890-91 ..	20·2 per cent	
1883-84 ..	26·0	,,	1891-92 ..	19·7	,,
1884-85 ..	22·6	,,	1892-93 ..	20·2	,,
1885-86 ..	19·9	,,	1893-24 ..	20·9	,,
1886-87 ..	18·1	,,	1894-95 ..	22·7	,,
1887-88 ..	16·9	,,	1895-96 ..	24·2	,,
1888-89 ..	17·0	,,	1896-97 ..	25·3	,,
1889-90 ..	18·4	,,	1897-98 ..	26·6	,,

The Returns of the Education Department given above refer to the whole of England and Wales, and are for the school years ending with August 31. The statistics of the London School Board are brought up to the year ending with Lady Day, 1899. They also illustrate the great advance that has been made in the teaching of Elementary Science, including Object Lessons, as a class subject. (Table C).

The work under the Evening Continuation Schools Code continues to progress, as will be seen by the following table, which gives the number of scholars taking scientific subjects in the year 1897-98 compared with those for the previous year. (See Table D).

The differences represent a total increase of 19,698, which is equivalent to 18·4 per cent. The only actual decreases are in Elementary Physics and Chemistry, Mechanics, Agriculture, and Navigation. It may be remarked that it is rather the practical than the theoretical subjects which are receiving less attention. The Mathematical subjects are still advancing rapidly, and so are Elementary Physiography and the Science of Common Things. The cognate subjects of Hygiene and Ambulance are evidently rising in popular favour. The same may be said of Horticulture. It would be interesting to know the relative proportions of young men and young women in

* Report of the Committee, consisting of Dr. J. H. Gladstone (Chairman), Professor H. E. Armstrong (Secretary), Professor W. R. Dunstan, Mr. George Gladstone, Sir John Lubbock, Sir Philip Magnus, Sir H. E. Roscoe, Professor A. Smithells, and Professor S. P. Thompson. Read before the British Association (Section B), Dover Meeting, 1899.

TABLE A.

Class subjects—Departments.	1891-92.	1892-93.	1893-94.	1894-95.	1895-96.	1896-97.	1897-98.
English	18,175	17,394	17,032	16,280	15,327	14,286	13,456
Geography	13,485	14,256	15,250	15,702	16,171	16,646	17,049
Elementary Science	788	1,073	1,215	1,712	2,237	2,617	2,143
Object Lessons	—	—	—	—	1,079	8,321	21,882

TABLE B.

Specific subjects—Children.	1891-92.	1892-93.	1893-94.	1894-95.	1895-96.	1896-97.	1897-98.
Algebra	28,542	31,487	33,612	38,237	41,846	47,225	53,081
Euclid	927	1,279	1,399	1,468	1,584	2,059	2,471
Mensuration	2,802	3,762	4,018	5,614	6,859	8,619	10,828
Mechanics	18,000	20,023	21,532	23,806	24,956	26,110	27,009
Animal Physiology	13,622	14,060	15,271	17,003	18,284	19,989	22,877
Botany	1,845	1,968	2,052	2,483	2,996	3,377	4,031
Principles of Agriculture	1,085	909	1,231	1,196	1,059	825	870
Chemistry	1,935	2,387	3,043	3,850	4,822	5,545	6,978
Sound, Light, and Heat	1,163	1,168	1,175	914	937	1,040	1,155
Magnetism and Electricity	2,338	2,181	3,040	3,198	3,168	3,431	3,905
Domestic Economy	26,447	29,210	32,922	36,239	39,794	45,869	51,259
Total	98,706	108,434	119,295	134,008	146,305	164,089	184,464

TABLE C.

Class subjects—Departments.	1890-1.	1891-2.	1892-3.	1893-4.	1894-5.	1895-6.	1896-7.	1897-8.	1898-9.
Elementary Science	11	113	156	183	208	246	364	322	310
Object Lessons	—	—	—	—	—	—	—	442	657

TABLE D.

Science subjects.	Number of scholars. 1896-97.	1897-98.
Euclid	1,036	1,525
Algebra	7,467	9,996
Mensuration	27,388	29,966
Elementary Physiography	3,712	4,807
Elementary Physics and Chemistry	3,135	2,902
Domestic Science	—	117
Science of Common Things	10,910	13,874
Chemistry	5,658	6,590
Mechanics	1,365	1,129
Sound, Light, and Heat	726	813
Magnetism and Electricity	3,834	3,967
Human Physiology	5,865	6,237
Hygiene	3,179	4,062
Botany	692	763
Agriculture	2,355	2,300
Horticulture	1,001	1,354
Navigation	68	37
Ambulance	9,086	13,030
Domestic Economy	19,565	23,271
Totals	107,042	126,740

these latter classes, but the Government returns do not supply this information. The only one of these subjects reserved exclusively for women is Domestic Economy. Domestic Science, as distinguished from the preceding, has only recently been formulated, and the first-fruits are only beginning to make their appearance in the column for the latter year. Unlike the day school work, which is largely governed by the requirements of the Education Department, and the preferences of managers and teachers, the Evening Continuation classes are to a great extent regulated by the public local demand, which rather seems to be for a continuation of the studies which have been begun in the Elementary Schools than for those practical subjects which are specially provided for by the Technical Instruction Act.

The London School Board have just passed a series of resolutions on the subject of the teaching of science in their schools, and amongst others that "Experimental Science instruction was desirable for girls as well as for boys:"—that "scholars of about Standard IV. should have an opportunity of doing some practical work themselves, such as linear (or other) measurement:"—and that "where some definite science is taught in the upper part of the school, the teaching of Experimental Science in the lower part of the school should lead up to it." The extension of the teaching of Science in the Board Schools has necessitated the Science demonstrators giving more and more attention to the preparing of the ordinary teachers for giving practical instruction in Science in their classes. These teachers have usually obtained certificates for one or more sciences under the Science and Art Department, but that does not necessarily qualify for the practical teaching of science according to modern views. Hence the need of the preparation above referred to. It would seem desirable that only those teachers who have some interest in, or aptness for, experimental work should be selected for this kind of training, and after having become thus qualified, they should be assigned, as far as possible, to this particular work. To carry this out more thoroughly, the board have decided "that Experimental Science classes for teachers be started under the Board in the autumn," and "that there be courses of Pedagogical Lectures to secure the practical teaching of Elementary Science, confined to teachers who have reached a certain standard of scientific knowledge of the subject on which the lectures are given."

It is to be hoped that under the newly constituted Education Department far more attention will be given than heretofore to improving the conditions under which science is taught in schools. Especially is it important that attention should be paid to the practical training of pupil teachers in the elements of scientific method. The time given to such work is altogether inadequate at present. But in some ways too much is often attempted, and from this point of view your Committee think it desirable to recall attention to the recommendations in the last paragraph of their report for 1897, as up to the present time no action has been taken by the Education Department.

The South-Western Polytechnic, Chelsea.—The Day College for Men, the Day College for Women, and the Evening Classes commenced on September 25th. Full particulars of all these classes may be obtained from the Secretary, Manresa Road, Chelsea.

SYNOPSIS FOR A DISCUSSION ON "LAWS OF SUBSTITUTION, ESPECIALLY IN BENZENOID COMPOUNDS."*

By Prof. HENRY E. ARMSTRONG, F.R.S.

1. In considering the formation of substitution derivatives from benzene and allied compounds, it is necessary to account for the very distinct behaviour of substances containing compound acid radicles (*i. e.*, radicles which in combination with OH form acids), which yield a large proportion of meta- derivative, whilst compounds containing other radicles yield ortho- and para-, and little, if any, meta- derivative. But no absolute distinction can be drawn, as much depends on the condition under which the change takes place, a considerable proportion of meta-derivative being obtained, for example, from aniline by nitrating it in presence of a large excess of sulphuric acid.

2. In the case of an amino-compound, it is possible to trace the action through a series of stages. Thus in sulphonating aniline, the sulphate first undergoes conversion into sulphamic acid, and this is converted into either ortho- or para-sulphonic acid, according to the conditions under which it is placed.

3. The process involved in the passage of sulphamic into sulphonic acid may be regarded as one of *isomeric change—i. e.*, it may be supposed that the SO_3H group wanders from one part of the molecule to another, without leaving the system and temporarily entering into some other form of combination.

In favour of this view is the fact that sulphonic acids are produced by the action of a sulphite on nitro-compounds under conditions under which the occurrence of independent sulphonation of the nucleus is, to say the least, unlikely; it is scarcely possible to doubt that in such cases the sulphamate is an intermediate product, as phenylhydroxylamine is converted into phenyl-sulphamic acid by the action of sulphur dioxide (Bamberger).

4. The possibility of isomeric change occurring in such a case cannot be denied in view of the fact that secondary nitrosamines, for example, are converted into para-nitrosamines by the action of acids, and of the many similar cases of change which have been brought to light in recent years by Bamberger, Hantzsch, and others.

In many such cases the change is so complete that it is impossible to believe that the radicle which wanders is first displaced from the molecule, and that the compound which is formed from it then enters into action with the molecule from which it was derived: for example, that in the case of the nitrosamines referred to the nitroso-group is split off in the form of nitrous acid, which then acts so as to form a para-nitroso-derivative; or, again, that when periodo-orthonitrophenetol is formed on nitrating orthiodophenetol the iodine becomes separated from the molecule and then attacks it afresh.

Moreover, bearing in mind the extreme readiness with which change takes place, for example, in the case of the formation of parachloracetanilide from the compound PHNClAc or of sulphanilic from phenylsulphamic acid, it is difficult to believe that the formation of the one compound is not a necessary stage in the formation of the other: the readiness with which the substituted benzenoid compound is obtained is so great that it is to be expected that both compounds would be formed together if they were independent products of the action of a single agent—just as, in fact, often happens in the case of para- and ortho-compounds.

5. It is very difficult to form any precise conception of the manner in which such "isomeric changes" are brought about. Something more than a mere interchange of position of the radicles is involved in them: some agent intervenes; but the operation of the agent is easily overlooked, as only a minute quantity suffices in many cases, the action being "fermentative" in character.

6. Very probably the peculiar structure of benzene and the tendency to pass from the centric to an ethenoid form and back again is the determining cause of the change; may be the function of the transforming agent is to bring about the change from the centric to a highly unstable ethenoid form, and the radicles change places at the moment that the agent is extruded from the compound and the system relapses into the centric form. A rough parallel is afforded by the well-known game of chairs, in which chairs are provided for all but one of a number of players; at a given signal all rise up and join their seatless companions, and then at another signal all seek to obtain seats: at this moment players are somewhat guided in their choice of places by the desire of certain couples to sit together; eventually the seats are again all occupied, but the order of the occupants is different, and as before one remains out.

7. Only primary and secondary amines can furnish sulphamic acids, and their formation is necessarily impossible in the case of tertiary amines; but it can scarcely be doubted that these are converted in the first instance into a sulphonated ammonium compound. The formation of *o*- and *p*-dimethylanilinesulphonic acids from dimethylaniline oxide and sulphur dioxide cannot well be otherwise interpreted, and in fact is so formulated by Bamberger:—

$$Me_2PhN(OH)_2+SO_2=Me_2PhN(OH).SO_3H.$$

8. Bamberger assumes that the formation of para-sulphonic acid from sulphamic acid is preceded by that of the ortho-acid, but in view of the stability of the ortho-acid this is improbable; it is to be expected that it would in a large measure persist under the conditions which, as a matter of fact, entail the production of only the para-acid. Thus, if acetanilide be carefully sulphamated, the product poured on to ice, and the solution then boiled, only sulphanilic acid is obtained; but if the solution of sulphamic acid in sulphuric acid be allowed to absorb water very gradually at a low temperature, a large proportion of ortho-acid is formed.

Apparently the ortho-acid is formed from the sulphamic acid if the sulpho-group be, as it were, let down gently; otherwise the para-acid is produced.

When the ortho- is converted into the para-acid by heating it with sulphuric acid, probably it is first hydrolysed, and sulphamic acid is then formed, and this in turn undergoes conversion into para-acid.

9. Whatever the changes involved in the production of ortho- and para-compounds, the nitrogen in amino-compounds clearly exercises both an attractive and a directive influence.

The nature, and more particularly the degree, of its influence depends, in a remarkable manner, on the nature of its immediate associates; hydrogen especially exercises an altogether peculiar influence on the course of substitution.

Nitrogen *per se* has little attractive or directive power, compounds such as azobenzene and diazobenzene bromide manifesting a singular inertness in presence of substituting agents; and it would seem that the more the influence of the hydrogen in amines is counteracted and the basic properties of the nitrogen neutralised, the more nearly do aminoid compounds generally approximate in their behaviour to simple azo-derivatives.

10. But not only does nitrogen cease to be attractive and directive when deprived of hydrogen and neutralised; it apparently even acquires inhibiting powers.

Thus dimethylanilineparasulphonic acid exchanges only a single atom of hydrogen for bromine, and the SO_3H group is displaced with difficulty by the further action of bromine. This behaviour is in striking contrast with that of sulphanilic acid, which is very readily converted into tribrom-aniline by the mere addition of bromine to its aqueous solution.

The effect of acid radicles is even more striking, and

* Read before the British Association (Section B), Dover Meeting, 1899.

somewhat different in character from that exercised by alkyls: thus when a single molecular proportion of bromine is added to a solution of acetylsulphanilic acid, less than half the acid is converted into the monobrominated acid; a major proportion simply exchanges the sulphonic group for bromine. Benzoylsulphanilic acid in like manner yields a mixture of monobrominated acid and parabromobenzanilid.

The stability of the brominated acid from *di*methylanilinesulphonic acid is perhaps accounted for—on the assumption that the attack proceeds from the nitrogen atom—by the fact that it forms a relatively stable dibromide. In the case of the *mon*acetylated acid, on the other hand, it may be supposed that the hydrogen in the amino-group is initially displaced, and that the bromine "wanders out" from this position partly into the ortho- and partly into the para-position.

11. When the conditions under which meta-derivatives are formed from amines are considered, it is clear that they are such as to favour the neutralisation of the basic properties of the amines, and to prevent the displacement of aminoid hydrogen.

The nitration of aniline in presence of excess of sulphuric acid may be taken as an example. A major proportion of the molecules being present as sulphate, the excess of nitric acid to the azo-radicle, and therefore to the system, is prevented: consequently no nitramine is formed, and a necessary stage in the formation of both *o*- and *p*-nitro-derivative is eliminated and their production prevented. On the other hand, as the action takes place at a low temperature, and nitric acid is present in its most concentrated form—perhaps as anhydride, in large measure—the conditions are such as to favour the attack of the benzenoid portion of the molecule, but only in the meta-position, the ortho- and para-positions being in a measure protected, owing to the inhibitive influence exercised by the fully saturated azo-radicle.

Although the basic properties of aniline are much reduced by the introduction of acetyl, acetanilid is still sufficiently basic to be attractive of nitric acid, and it therefore undergoes conversion into nitramine, and subsequently into ortho- and para-nitro-derivative.

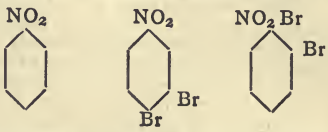
Benzanilid being far less basic, is only very partially acted upon in this manner; the benzenoid portion of the molecule is therefore preferred for attack, and consequently a considerable number of molecules become meta-nitrated.

Dimethylaniline is converted entirely into para-acid when sulphonated by ordinary sulphuric acid at about 180°, or by chlorosulphonic acid; but when carefully sulphonated by fuming acid it yields a large proportion of meta-acid. Doubtless, in this latter case, the conditions correspond to those pictured in the case of benzanilid undergoing nitration. That the formation of meta-acid is a consequence of the sulphate undergoing sulphonation, and is not merely due to the use of the more powerful agent SO_3, clearly follows from the fact that so powerful an agent as SO_3HCl converts dimethylaniline only into para-acid.

The behaviour of acetanilid and benzanilid towards forming sulphuric acid is precisely similar to their behaviour towards nitric acid—the former gives only *o*- and *p*-acid, the latter a considerable proportion of meta-acid. Probably both are initially converted into sulphamic acid; but the acid formed from the latter being less prone to undergo isomeric change, it becomes in part meta-sulphonated.

12. In the case of compounds other than amines which afford meta-derivatives, it may be supposed that the radicle is both unattractive and "ortho-para inhibitive," and that consequently opportunity is given for the attack to become concentrated upon the benzenoid portion of the molecule in the meta-position.

As in such cases some proportion of *o*- and *p*-compound is usually obtained, it is necessary to assume—if the radicle be regarded as altogether unattractive—that the benzenoid portion of the molecule is open to attack at several points; indeed, this may be more or less true of all compounds. Thus it may be supposed that when nitrobenzene is brominated two compounds are initially formed, thus:—



The 1 : 2 compound being a very minor product, but little ortho-compound is eventually obtained, and, owing to the unattractive and inhibitive influence exercised by the NO_2 group, bromine is chiefly separated from the para-position of the 3 : 4 compound; consequently but little para-derivative is formed.

13. The phenols in many ways closely resemble the amines in their behaviour towards substituting agents. The hydrogen in association with the oxygen clearly plays an important part; in fact, the extreme activity of phenols is probably, in large measure, due to the presence of hydrogen in the extra-benzenoid radicle, as in the case of the amines, but the part which the hydrogen plays cannot at present be at all clearly made out.

By displacing the hydroxylic hydrogen by alkyls, effects are produced very similar to those observed in the case of amines. Thus phenol-parasulphonic acid, like sulphanilic acid, at once exchanges two atoms of hydrogen for bromine, and then quite readily exchanges the SO_3H group for bromine. But the acids obtained by introducing methyl, ethyl, or benzyl in place of the hydroxylic hydrogen yield only monobrominated acids, which on further treatment exchange the SO_3H group for bromine; and this action takes place only partially, as a large proportion of the acid directly exchanges the SO_3H group for bromine, a monobrominated compound being formed, just as in the case of acetyl- and benzoyl-sulphanilic acid.

Benzoyl appears to exercise a very remarkable inhibitive effect, as preliminary experiments show that benzoylated phenolparasulphonic acid remains unattacked by bromine under conditions which involve the conversion of the unbenzoylated acid into tribromo-phenol.

It may therefore be supposed that oxygen in phenols, being possessed of residual affinity, exercises an influence on substitution similar to that which nitrogen exercises in amines; and as it has no basic qualities, it is difficult, if not impossible, to deprive it of its activity, and consequently of its para-ortho-orienting power: hence it is that phenols do not yield meta-derivatives. Should conditions be discovered which will make it possible to hold the activity of oxygen in check, it will probably be found possible to directly prepare meta-phenolic derivatives.

14. Sulphur, whilst resembling oxygen, apparently has a still stronger inhibitive influence. Thus phenyl ethyl thio-ether may be para-sulphonated without difficulty, but para-bromophenyl ethyl thio-ether is not sulphonated either by sulphuric or by chlorosulphonic acid, although the corresponding oxygen compound is very readily acted on.

15. The behaviour of halogen derivatives may be correlated with that of phenols, or rather with that of their ethers, especially in view of the existence of compounds such as phenyl iodosochloride, $PhICl_2$. On the assumption that the residual affinity of iodine was satisfied in this compound, it appeared not improbable that it might furnish a meta-sulphonic acid. It is sulphonated without difficulty, but the product is highly chlorinated, and its nature has yet to be ascertained.

16. The hydrocarbons homologous with benzene are the most difficult group to discuss. The paraffinyl radicle certainly exercises a directive effect; whether it is in any way attractive is open to question. Bearing in mind the inactivity of the paraffins, it is difficult to believe that the radicles derived from them are possessed of sufficient

activity to account for the striking readiness with which the homologues of benzene are acted upon in comparison with benzene. The introduction of hydrogen radicles seems, in fact, to produce a fundamental modification in the centric complex, the behaviour of hydrocarbons such as mesitylene being ethenoid rather than benzenoid; and from this point of view it seems probable that the derivatives of benzenoid hydrocarbons are formed more in accordance with the process formulated in paragraph 12.

The fact that when the paraffinyl radicle undergoes chlorination or oxidation, for example, the attack, as a rule, takes place at the point of attachment is proof that, if not itself attractive, it immediately adjoins the centre of attraction; and it is possible that initially some change takes place in which both radicles are involved.

OXIDATION IN THE PRESENCE OF IRON.*

By HENRY J. HORSTMAN FENTON, M.A., F.R.S.

The remarkable influence which iron exerts upon the oxidation of certain organic substances was first pointed out by the author in 1876 in the instance of tartaric acid. This observation has since been fully investigated, and has led to an extensive study of the behaviour of various other substances under similar conditions of oxidation and of the resulting products (Fenton, Chem. News, 1876, xxxiii., 190; 1881, xliii., 110; *Trans. Chem. Soc.*, 1894, 899; 1895, 48 and 774; 1896, 546; 1897, 375; 1898, 71 and 472, &c. Fenton and Jackson, 1899, 1 and 575; Cross and Bevan, 1898, 463; 1899, 747; Morrell and Crofts, 1899, 786; Martinon, *Bull. Soc. Chim.*, 1885, ii., 23, 196; Ruff, *Ber.*, 1898, 1573; 1899, 550.

The peculiar advantage of the method consists in the fact that the extent of oxidation may be regulated, and consequently that it is often possible to obtain products of limited oxidation which cannot be prepared in any other way.

Hydrogen peroxide is the most efficient oxidising agent for the purpose, although others may sometimes be substituted. The iron, which is essential to the process, must in almost all cases be present in the ferrous condition; its proportion, however, bears little if any relation to the yield.

With regard to the general nature of the oxidation products, it may be observed that in the case of tartaric acid the change may be represented as a removal of the two non-hydroxylic hydrogen atoms; in the polyhydric alcohols the (primary) CH_2OH groups are attacked in preference to the (secondary) CHOH groups, whilst in certain carbohydrates the CHOH group adjacent to an aldehyde group appears to be oxidised; the aldehyde group itself is remarkably resistant. In the benzenoid compounds H is usually replaced by OH, and a similar behaviour would appear to obtain in the furfurane derivatives. In all cases it might be assumed that the initial result is the replacement of H by OH, tartaric acid, for example, being supposed to give, in the first instance, trioxysuccinic acid.

The part played by the iron in these changes is still a matter for discussion. In a previous note (*Proc. Chem. Soc.*, 1898) a provisional theory was proposed, in which it was suggested that the ferrous iron first replaces non-hydroxylic hydrogen and is subsequently oxidised; and it is certainly remarkable that in the case of every substance found to be sensitive to this reaction, non hydroxylic hydrogen is present, associated in almost every case with alcoholic hydroxyl.

With a view of throwing further light upon the general nature of this oxidation process, the author is at present studying a variety of substances of typical constitution, and the following is a brief account of results which have recently been obtained with certain acids:—

Tartronic acid gives a large yield of mesoxalic acid. The hydrazone of the latter acid separates at once on the addition of phenylhydrazine hydrochloride, and it is probable that the process may be found advantageous for the preparation of the free acid, especially as the production of tartronic acid has been much simplified (*Trans. Chem. Soc.*, 1898, 72). This transformation has not hitherto been effected, although the converse operation—the reduction of mesoxalic to tartronic acid—is well known.

Lactic acid, in a similar manner, yields pyruvic acid, but the operation requires especial care.

Glyceric acid, when oxidised in the same way, produces a substance having strong reducing properties, and which gives an intense violet colour with ferric salts in the presence of alkalis. On treatment with phenylhydrazine acetate an osazone is produced which crystallises in golden needles, melts at 203°, and gives a beautifully crystalline sodium salt and pyrazolon. It appears to coincide in every way with the osazone of oxypyruvic acid, $C_{15}H_{14}N_4O_2$, which was obtained by Nastvogel from dibrompyruvic acid (*Annalen*, 248, 85), and by W. Will from the product of the action of soda on collodion wool (*Ber.*, 1891, 400). The substance produced in the present case may therefore be (1) oxypyruvic acid, (2) the semi-aldehyde of tartronic acid, or (3) the semi-aldehyde of mesoxalic acid.

Malic Acid.—Judging from previous results, it was to be expected that this substance would yield oxal-acetic acid, and it is possible that such may be the result in the first instance, since, on treatment of the product with sulphuric acid, a certain amount of pyruvic acid is obtained. If, on the other hand, the product be treated with phenylhydrazine acetate, a substance is obtained which crystallises in golden prisms, melts at 216—218°, and gives crystalline sodium and potassium salts.

The above-mentioned products are being fully investigated, and the results will shortly be published.

The author wishes to express his thanks to Mr. H. O. Jones, B.Sc., for the valuable assistance which he is giving in this portion of the work.

* Read before the British Association (Section B), Dover Meeting, 1899.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending August 31st, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 11th, 1899.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The drought in the Thames Valley during August has been less severe than during the two previous months. The total rainfall at Oxford in August was 1·80 inches, the average for the last thirty years being 2·32 inches. This makes a deficiency of only 0·52 inch, compared with deficiencies of 1·06 inches for June and 1·36 inches for July. The total deficiency for the year is now 3·63 inches, or 22·6 per cent.

Our bacteriological examinations of 382 samples have given the results recorded in the following table; we have also examined 49 other samples, from special wells, standpipes, &c., making a total of 431 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	410
New River, filtered (mean of 76 samples) ..	12
Thames, unfiltered (mean of 26 samples) ..	2269
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 206 samples)	31
Ditto ditto .. .. highest	289
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	863
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	12

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

ON THE ESTIMATION OF CHLORINE, BROMINE, AND IODINE WHEN MIXED.

By J. BOUGAULT.

A considerable number of methods have been proposed for the separation one from the other of chlorine, bromine, and iodine, with a view to their separate estimation. These methods, fairly practicable in the case of iodine, are much more delicate of application when we have to deal with the separation of chlorine from bromine, on account of the so closely allied chemical affinities of these two elements. Further, text-books generally recommend as the best an indirect method which comprises the three following operations:—1. Precipitation by nitrate of silver and weighing the mixed precipitate; 2, Conversion of the whole of the argentic precipitate into chloride of silver and weighing the chloride of silver formed; 3. Separation of the iodine, either by precipitation with chloride of palladium, or by setting it free by means of an oxidising agent (MnO_4K, CrO_4K, NO_2H, &c.), and removing it by means of sulphide of carbon. In the case of the presence of two halogens only, it is evident that the two first operations will suffice.

I thought it would be possible to advantageously substitute, for the second operation, reduction of the mixed precipitate of the haloid salts of silver by reduction with zinc and sulphuric acid, and weighing the reduced silver. This modification rests, as will be seen, on a well-known reaction; but the simplicity of its execution, the accuracy of the results, and the fact—which has surprised me not a little—of not finding it described anywhere, have caused me to call attention to it.

The following is the best method of procedure:—

We must first make quite certain that the zinc used is completely soluble in dilute sulphuric acid; granulated zinc fulfilling this condition, described as chemically pure, can be obtained commercially

We then weigh very exactly a quantity of argentic precipitate of from 0·5 grm. to 1 grm. in a small precipitating glass, and add about 50 c.c. of dilute sulphuric acid (50 grms. SO_4H_2 in 500 grms. of water). We then take a quantity of chemically pure zinc about equal to that of the argentic precipitate, and add it in small portions of 0·15 grm. to 0·2 grm., waiting for one portion to be almost dissolved before adding the next. In a very short time the whole of the argentic precipitate is brought to the state of metallic silver; we allow the excess of zinc to become completely dissolved (this is absolutely indispensable); we must make certain that this takes place by making sure that the solution contains no solid particle giving rise to a disengagement of gas, no matter how feeble; any particle of zinc would thus be easily detected. To make still more certain, it is as well to leave the mixture for a few hours with occasional stirring. When all the zinc is dissolved, we filter and wash with distilled water.* The precipitate is dried in the oven, calcined in a tared crucible, and weighed; the increase in weight of the crucible, less the weight of the ash of the filter, gives the weight of the reduced silver.

I have carried out this operation on chemically pure chloride, bromide, and iodide of silver prepared specially for verifying the accuracy of the process, and obtained the following results:—

				Theory.
0·521 grm.	AgI	gave me	0·2392 of silver.	0·2394
0·545 ,,	AgCl	,,	0·4104 ,,	0·4102
0·678 ,,	AgBr	,,	0·3898 ,,	0·3894
0·3825 ,,	AgCl	,,	0·4698 ,,	0·4698
0·3960 ,,	AgI	,,		

I would add that I have had occasion to apply this method to the estimation of chlorine and of iodine in substances containing from 40 to 50 per cent of iodine, with only 3 to 6 per cent of chlorine; the results obtained were very satisfactory.—*Journ. de Pharm. et de Chim.*, Series 6, vol. x., No. 1.

DETECTION AND COLORIMETRIC ESTIMATION OF SMALL QUANTITIES OF IODINE IN ORGANIC MATTERS.

By PAUL BOURCET.

The material in which we wish to search for iodine is, according to its nature, finely chopped up or powdered, it is then moistened with a dilute solution of potash completely free from iodine, then dried in the oven at 100°. The dried mass is again finely powdered, then melted with potash free from iodine in an iron crucible, or, better still, a nickel one.†

The fusion ended, the mass is allowed to cool and is then exhausted with boiling distilled water until the filtered washings are no longer sensibly alkaline. The solution thus obtained is reduced by evaporation to one-half its original volume. To the cold solution we add, very gradually, pure sulphuric acid diluted with five times its weight of distilled water, taking care to avoid all heating, and, if necessary, even cooling down the vessel in which the saturation is effected. When the solution is neutral, a few drops of a solution of potash free from iodine are added to make it slightly alkaline, and then, with continued stirring, one-half its volume of alcohol at 95° is slowly added. The greater part of the sulphate of potash is thus precipitated in the state of a fine powder, which is drained on a filter-pump and washed with alcohol at 30 per cent, which carries off the mother-liquors

* The filtered liquid and the wash waters contain the whole of the hydrochloric, hydrobromic, and hydriodic acids formed during the reaction. By precipitating with nitrate of silver we can recover the argentic precipitate used integrally.

† When we use an iron crucible, we should commence by melting the potash free from iodine, and rinsing the whole of the interior surface of the crucible with the melted potash. We thus remove the small quantity of iodine which iron crucibles may sometimes give up to the potash the first time they are used for such a fusion.

with which it is impregnated. The filtrate is evaporated down to one-third of its original volume, and when cool is treated with alcohol at 90°. A further quantity of sulphate of potash is precipitated; this is drained and washed with alcohol at 30 per cent, as before. By repeating the concentration of the filtrates and their precipitation by alcohol several times, we finally eliminate all, or nearly all, the sulphate of potash, while the iodine—if there is any present—is concentrated in the alkaline liquids soluble in alcohol.

The last solutions thus obtained are evaporated to dryness in a nickel or porcelain crucible, and the residue submitted to gentle heating over the flame to destroy the small quantity of organic matter which might still be present. On cooling, it is taken up with a small quantity of warm distilled water and filtered; it is in the few c.c. of solution thus obtained that the iodine is displaced by nitrous fumes in the presence of sulphide of carbon, and is then estimated colorimetrically according to the method given by MM. Rabourdin and Nicloux.

We are confident by this method we should be able to recover the whole of the iodine added to an organic material nitrated or not, but not iodised.

Thus, for example, taking two samples of sugar free from iodine, each weighing 100 grms., to which 1/30th and 2/30ths of a m.grm. of iodine in the form of an alkaline iodide had been added, we found, after having treated them both according to the method we have just described, that the residue of the second sample of sugar contained double the quantity of iodine found in the residue of the first, and that colorimetrically the latter agreed with a solution in which we had previously dissolved 1/30th of a m.grm. of iodine.

This method of detecting and estimating iodine has enabled us to determine very small quantities of iodine in a certain number of alimentary materials the weights of which varied from 50 grms. to 1 kilogrm. Our qualitative and quantitative estimations of the iodine in these substances form the object of another research which we have not yet completed. For the present, as an example, we give the results which we found with various kinds of fish.

	Iodine per kilogrm. M.grm.
Smoked herring (eggs)	0·8
" " (soft roes)	0·6
Do. (whole)	1·7
Do. (whole)	1·8
Do. (whole)	2·0
Portuguese oysters	1·3
Fresh ray	0·2
Whiting	0·3
Mackerel	0·3
Sardines (salted)	0·6
Gurnet	1·2
Mussels	1·9
Cod (salt)	1·2
Coal fish (intestines)	2·4
Do. (flesh)	0·9
Shrimps	0·7
Periwinkles	0·75
Eel	0·8
Pike	0·3
Roach	1·2
Gudgeon	0·12
Bream	1·2
Sole	0·8
Salmon (head)	1·4
Salmon trout	0·1
Carp	0·6
Mullet	0·6
Ling	1·2

We have made a large number of other estimations which lead to general deductions which we shall make known later on.—*Bull. Soc. Chim.*, Series 3, xxi., No. 11.

ANALYTICAL METHODS FOR DISTINGUISHING BETWEEN NITROGEN OF PROTEIDS AND NITROGEN OF SIMPLER AMIDES OR AMIDO-ACIDS.

By J. W. MALLET,
Professor of Chemistry, University of Virginia.

(Continued from p. 119).

Methods of Separating Nitrogen.

A brief notice of several methods of separating nitrogen will afford means of comparison. The phospho-tungstic method which was especially investigated is treated more fully than the others.

Dialysis.

The attempt to separate such proteids as are soluble in water from the simpler amides intentionally mixed with them by applying Graham's method of dialysis was made with no great hope of success. It is, of course, well known that the amorphous proteids in solution exhibit as a class a very small degree of diffusive mobility, while the crystallisable, simpler amides diffuse through a porous septum, as of parchment paper, with much greater rapidity. But separation based on this difference can never be complete. Only a part of the more diffusible material can be obtained in the water on the opposite side of the diaphragm from the mixed solution, and that a large part shall be so obtained requires that the volume of water used shall be large as compared with the volume of the solution. Moreover, the absolute volume of the solution itself must be large where amides of but slight solubility—such as tyrosin—are present, in order that they may not be left behind in the undissolved state. But the time required for dialytic separation extends to many hours, or even several days, and during such protracted exposure to the air and to common atmospheric temperature weak solutions of the proteids readily undergo chemical change. Again, it is to be remembered that the peptones, classed with the proteids, are diffusible in much higher degree than natural proteid material prior to its exposure to the action of the digestive fluids. This fact has well-known physiological importance in its bearing on the preparation of proteid food for absorption from the alimentary canal, but in analysis it tends to confound the particular group of the peptones with the simpler amides. In the recovering from weak solutions of small quantities of dissolved substances by the evaporation of large amounts of water, further chemical change of the substance recovered is likely to vitiate the results.

Nevertheless, some twenty or more experiments were carried out with dialysers made from the tubes of parchment paper which can now be bought in Germany. Cylinders of about 6 inches long were cut from these tubes, and closed at one end by thin glass, carefully tested as to freedom from holes, and immersed in water contained in ordinary glass beakers. A fairly clean separation was obtained of leucin, aspartic acid, and creatin, from solutions to which had been added egg or serum albumen, the diffusate being in each case evaporated at a moderate temperature over the water-bath, and the residue weighed. But the process of diffusion was inconveniently slow, and less satisfactory results were obtained when the dialysed solution was made more complex by the addition of other substances.

Subsequently the writer's attention was attracted by the paper of Charles J. Martin (*Journ. Physiol.*, 1896, xx., 364—371), on the use for a like separation of a Pasteur filter in the pores of which a film of silicic acid has been deposited, the filtration being brought about under pressure. It has been practicable to make only two or three experiments in this way. The method is decidedly promising, but it seems more likely to be useful in the purification of substances in quantity than as a process of analysis. With small quantities of material it

can hardly be made available for regular laboratory work in connection with nutrition investigations. It involves the same difficulty as any other form of dialysis in cases in which the proteoses and peptones are present.

Interaction with Nitrous Acid.

It was hoped that by varying the conditions of experiment with this reagent some characteristic differences of behaviour might be observed as regards the evolution of elementary nitrogen.

The most advantageous mode of producing nitrous acid in definite amount was found to consist in bringing together, along with the material to be acted upon, pure silver nitrite and a hydrochloric acid solution of known strength. The action took place in a glass flask of about 100 c.c. capacity, closed by a stopper through which passed through the long neck of a cylindrical funnel holding about 60 c.c., the neck having an interior diameter of but 1 m.m., and separated from the wider cylindrical reservoir by a well-ground glass stopcock. There also passed through the same stopper the stem of a thermometer reading to one-tenth of 1 degree with accuracy, a small tube with stopcock for the introduction of gas to displace the air of the apparatus, and a second small tube to carry off the nitrogen evolved. The capacity of the flask was carefully gauged with the tubes and thermometer in position and the stopper inserted to a marked depth in the neck, so that after the introduction of any known volume of solid or liquid material a simple subtraction would give the volume of gaseous matter remaining included. A gas-measuring cylinder, connected with the flask by a tube of very small bore and immersed in water in a larger cylinder which could be raised or lowered, provided for collecting and measuring the evolved nitrogen. The flask was supported in a water-bath, so that it could be heated or cooled at pleasure.

In order to give time for action upon the organic material under experiment, and to keep down to conveniently small limits the evolution of nitrogen dioxide, it was found important to work with the nitrous acid in a sufficiently diluted condition. With the same object in view it was found desirable to raise the temperature of the flask very gradually. In carrying out an experiment the particular amidic or proteid material was finely pulverised, weighed off, and introduced into the flask, either in the dry state or with as little recently boiled water as possible, and with the necessary amount of silver nitrite, as a fine crystalline powder. This powder was contained in a small, thin, glass cylinder, which could be easily upset in order to mix its contents with the other materials in the flask. A current of nitrogen gas was next run through the flask until all air was expelled. In the case of substances dissolving in water with difficulty the flask was now allowed to stand closed for some time to permit of solution taking place. Communication was established with the gas-measuring cylinder, and the proper quantity of standard hydrochloric acid, made by diluting very strong aqueous acid with boiled water and kept in small well-closed bottles, was gradually introduced through a funnel with capillary bore. Care was taken that no air was admitted. After all action in the cold had ceased the temperature of the flask was gradually raised by means of the water-bath up to a maximum of about 96° or 97° C. As soon as all action was over and the apparatus had cooled down to atmospheric temperature the flask was nearly filled up with recently boiled water, introduced through the capillary funnel, and a small measured volume of nitrogen was run in to displace any remaining nitrogen dioxide. The gas in the measuring cylinder was then treated with oxygen in sufficient excess to dispose of all nitrogen dioxide, and with caustic potash and pyrogallol to remove excess of oxygen. After standing at rest for some time the gas was measured, due allowance being made for the nitrogen present in the flask at first and for the small additional amount afterwards introduced. Of course, the proper corrections for pressure, temperature, and tension of aqueous vapour, were made in connection with all the measurements of gas, and the quantity of nitrogen obtained was divided by 2, one half being yielded by the organic substance and the other by the nitrous acid.

With a view to guard against the retention of any nitrogen in the form of di-azo derivatives from amides, a moderate excess of hydrochloric acid was used. In the case of kreatinin the results are complicated by the formation of the supposed nitroso-compounds observed by Dessaignes. With several of the proteids the bright yellow colour of the so-called xantho-proteic acid was well-marked, as the consequence, doubtless, of the action in the flask of nitric acid produced by the breaking up of nitrous acid into nitric acid, nitrogen dioxide, and water. Too little is known of the yellow substance formed, Mulder's xantho-proteic acid, to indicate how far its nitrogen comes from the proteid and how far from the nitric acid, or in what direction or to what extent its formation may influence the amount of elementary nitrogen given off. In the case of proteid solutions coagulable by heat, it was manifestly important to allow the action of the hydrochloric acid on the silver nitrite to become complete below the temperature of coagulation, as otherwise silver nitrite was entangled in clots of the coagulating proteid. In some, at least, of these experiments, it seemed probable that a part of the nitrogen dioxide given off, and perhaps of the free nitrogen, was due to the reducing action of the carbon or hydrogen of the organic substance upon nitrous or nitric acid, and not solely to the normal interaction of nitrous acid and the amidogen radicle present.

The process was varied, not only in respect to the temperature applied, but also, within moderate limits, in respect to the pressure on raising or lowering the gas measuring-tube in the water. It was further varied by increasing the proportion of nitrous acid to different extents in excess of the theoretically necessary amount.

In all some fifty or sixty experiments were made. In a number of cases the simpler amidic compounds gave a fair approximation to the quantity of nitrogen theoretically to be expected from them, though even with such substances as leucin, asparagin, and aspartic acid, the results were not as sharp as the claims of Sachsse and Kormann would lead one to suspect. One of the best experiments yielded for aspartic acid 9·57 per cent of nitrogen, instead of the 10·53 per cent actually present. Kreatin did not give one-half of its nitrogen, as has been heretofore recorded as the fact, but a somewhat nearer approach to one-third,—10·19 per cent as against 32·06 per cent,—the probability of which result is indicated by the accepted structure of the molecule. In all cases the proteids gave some nitrogen, but the proportion was much smaller than from the simpler amides, and varied much more with the precise conditions of temperature, pressure, and strength of solution used. In one experiment serum albumen gave but 2·68 per cent, and in another but 2·92 per cent was obtained from hæmoglobin.

On the whole, the indications pointed to the simpler amides and amido-acids being most easily decomposed by nitrous acid, the proteoses and peptones perhaps next, and the proteids proper least. But no differences were observed upon which any useful analytical process of separation or distinction could be based. Experiments made in this way are, moreover, troublesome, and require strict observance of the necessary precautions to avoid error from introduction of air into the apparatus and its action on nitrogen dioxide.

Interaction with Potassium Permanganate in presence of Free Acid or Alkali.

THE writer had not much hope of obtaining useful results by this method, in view of former experience gained in connection with the extended research upon the determination of organic matter in drinking water carried out many years ago for the U.S. National Board of Health,

of which the results were published in the annual report of that Board for 1882. Still, as the work then done was upon extremely dilute solutions, comparable in respect to the amount of organic matter present with natural potable waters, it seemed possible that results not altogether of the same sort might be obtained with solutions of greater concentration. Hence some thirty or forty experiments were made with permanganate strongly acidified with sulphuric acid, and a rather larger number with the same salt after potassium hydroxide had been added in about the same proportion as is usual for the Wanklyn, Chapman, and Smith so-called albumenoid-ammonia process. In the former set of experiments the amount of oxygen withdrawn from the permanganate, and in the latter set the amount of ammonia produced, were determined. In both cases the reactions were carried out at various temperatures up to the boiling-points of the several liquids.

Some difference was observable in the results obtained with the comparatively strong solutions used, such difference being more notable for alkaline than for acid permanganate. But in the main these results only confirmed the conclusions arrived at in the earlier research. The effect of the reagent employed is imperfect, and varies much with the nature of the individual organic materials tested; much, also, with the conditions of the experiment and with the rate at which the action proceeds. No valid evidence is obtained in support of Wanklyn's view that simple and definite fractions of the total nitrogen present are evolved as ammonia on treatment with alkaline permanganate.

Some special difficulties and sources of error already known were re-observed; as, for instance, the continuous evolution of ammonia by boiling many organic substances with alkaline permanganate until distillation has practically brought the contents of the retort to dryness, without all of the nitrogen present having been given off. And some other causes of trouble were noticed; as, for instance, the loss of oxygen given off as such from a strong and acid solution of permanganate on standing in a heated condition irrespective of action on the organic matter present.

The general tenour of the results in the case of the nitrogenous substances treated pointed to more energetic and extensive action of permanganate in alkaline than in acid solution; also to more extensive action on the simpler amidic compounds than on the proteids. But notwithstanding sundry variations of method as to strength of the reagent solutions, proportion of reagent to organic material acted on, temperature, and time of action, no indication was obtained of any valid basis for distinction in analysis between the two classes of nitrogenous material studied.

Interaction with Sodium Hypobromite.

This reaction is so frequently used for the appoximate determination of urea (carbamide), while its results with other amides have been so scantily examined and almost no facts bearing on its relation to the proteids have been recorded, that a good deal of interest was felt in examining it somewhat extensively with the two classes of materials which were studied.

The solution of bromine was prepared with 240 grms. of potassium bromide, 200 grms. of free bromine, and enough water to make up a litre. The solution of caustic soda was made with 340 grammes of pure sodium hydroxide to the litre. These solutions were preserved in separate bottles, and equal volumes of the two were mixed just before using. When undiluted the mixture represented 0·1 grm. of originally free bromine to each c.c., and was in most of the experiments used of this strength; but various dilutions were also employed, being made by additions of water in definite amount.

The apparatus with which the reaction was carried out was essentially the same as that adopted for the experiments with nitrous acid, save that the small tube was omitted which was intended to introduce an inert gas to displace air from the apparatus, this precaution being unnecessary in the hypobromite experiments.

Nearly eighty experiments were made, varying the conditions as to temperature from that of the atmosphere, usually 15°to 20°, up to 96° to 98° C., as to pressure within the limits allowed by the immersion of the gas-measuring cylinder, and as to time from fifteen or twenty minutes up to five or six hours.

In some cases the results obtained were in agreement with those of the few hitherto recorded experiments—as, for instance, aspartic acid gave no nitrogen, as was found to be the fact by Allen and Tankard. In other cases there was disagreement with some of the published statements and confirmation of others. Thus, Allen and Tankard obtained no nitrogen from glycosin (A. H. Allen, "Commercial Organic Analysis," 1896, vol. iii., Part 3, p. 275), and Tankard none from asparagin,* while Œchsner de Coninck reported both these substances as acted on (by sodium hypochlorite) when gently heated, nitrogen gas being evolved (*Comptes Rendus*, 1895, cxxi., 893, 894; *Journ. Chem. Soc.* (London), 1896; Abstracts, *Org. Chem.*, p. 282). The writer obtained from glycocin 4·2 per cent of nitrogen instead of 18·67 per cent as required by the formula,† and from asparagin 11·12 per cent instead of 18·67 per cent, the amount calculated, taking account of the presence of a molecule of water of crystallisation.

In a number of cases the quantity of nitrogen evolved from an amide or amido-acid of known constitution seemed to represent a simple fraction of the total quantity contained in the material operated on, and it might not unnaturally be suspected, as in some of the cases reported by Allen and Tankard, that one-fourth or one-half to two-thirds of the whole quantity was liberated. Thus in one experiment leucin gave 2·58 per cent of nitrogen instead of 10·69 (calculated), or about one-fourth; in another, kreatin gave 21·96 per cent instead of 32·06 (calculated), about two-thirds: and in another, hypoxanthine gave 18·80 per cent instead of 41·18 (calculated), which might mean one-half—two atoms out of four. But it is not believed there is any more real significance in these approximations to definite fractional parts of the nitrogen being evolved than in the similar approximations to which Wanklyn drew attention in connection with his so-called albumenoid-ammonia process. His conclusions have been shown to be entirely erroneous. Different figures could be obtained from the same materials acted on by varying the conditions of the experiment, and in some cases there was no really sharp ending to the reaction, traces of gas continuing to be slowly given off for hours after the main portion had been collected. Moreover, while our knowledge of the constitution of kreatin would make it not improbable that two atoms of nitrogen out of three should be liberated or two out of four in the case of hypoxanthine, there is no similar ground for any expectation that leucin, containing but one atom of nitrogen in the molecule, should yield one-fourth; or glutamic acid, also with but one atom, should yield something like one-fourth (2·56 per cent instead of 9·52 calculated).

The researches of S. Hoogewerff and W. A. van Dorp have shown that numerous definite products other than elementary nitrogen may be formed by the action of alkaline hypobromites upon amides and amido-acids, especially those containing cyclic nuclei. In several of the writer's experiments—as, for instance, with alinin among the simpler amido-acids, and with a sample of globulin among the proteids—a crystalline residue separated out in the flask on cooling. This residue was not examined further than to determine qualitatively that it contained nitrogen. The proportion borne by the nitro-

* Possibly the solutions were not heated.

† In Watts's "Dictionary of Chemistry," revised edition by M. M. Pattison Muir and H. F. Morley, vol. ii., p. 627, it is stated, on the authority of Denigès (*Comptes Rendus*, cvii., 662), that with sodium hypobromite nitrogen is evolved from glycocin.

gen left in such fixed residual products to that collected as gas evidently varied with the conditions of the particular experiment, as well as with the nature of the substance acted on.

All the proteids and analogous materials treated gave some gaseous nitrogen. For the most part the amount was about two-fifths of the whole amount present; but occasionally a larger proportion, as in one experiment with globulin just about one-half, and in another with myosin about three-fourths. In this last case the action was allowed to go on at a high temperature for a time much longer than usual. The remarks already made in regard to the simpler amidic substances, as to modification of results by variation of the conditions of experiments, fully apply also to the experiments with proteids and their congeners. The lack of sharpness of ending to the reaction was more noticeable with the latter class of materials than with the former.

Although these experiments with alkaline hypobromite were interesting, and occasionally offered points which might repay further investigation, they did not, taken altogether, afford any satisfactory basis for distinguishing in analysis between the classes of materials to be studied in contrast with each other.

(To be continued).

NOTICES OF BOOKS.

The London Water Supply. By Arthur Shadwell, M.A., M.B. (Oxon.), Member of the Royal College of Physicians. London, New York, and Bombay: Longmans, Green, and Co. 1899. Pp. 272.

The London water supply has attracted considerable attention of late years, more especially since the London County Council commenced its attack on the London water companies nine or ten years ago.

The author has treated his subject in a masterly manner, and has traced the formation and growth of the water companies from their inception many years ago to the present time. He points out very pertinently that "for years the water companies have been a common cock-shy for every kind of ridicule and abuse." Last autumn the newspapers, mostly of a certain political complexion, were full of insults, spiteful innuendoes, and silly sarcasms against the officials of the East London Company, as if they were personally responsible for the existence of the concern, which was established by Act of Parliament before they were born.

Many people think that if they throw enough mud some is sure to stick, and it has been stated so many times that London is abominably served with water, that it is scanty in quantity, bad in quality, and very dear, that we drink "diluted sewage," &c., that doubtless some people think this is all true.

The author has carefully gone into figures of the quantity, quality, and cost of London water as compared with most of the large towns in England. A few of these figures will not be uninteresting. First, with regard to quantity; out of a list of twenty-four of the largest towns in England there are only three, viz., Brighton, Plymouth, and Hull, which have a greater daily supply per head than London. Of the three above-mentioned towns each has an average daily supply of 43 gallons per head, that of London being 38½ gallons; most of the other twenty-one towns have a considerably smaller supply.

With regard to quality, the supplies of so few towns are systematically examined as that of London is, that figures are not easy to procure; but compared with figures obtained from Birmingham and Glasgow, the water from these two model municipalities is seen to contain considerably more organic matter than London water, while the death rate from typhoid in Glasgow is double that of London.

A table given by the author of the cost of the water supply in thirteen of these towns shows that the poorer consumers in London enjoy a very considerable advantage over those in the provinces; the highest charge in London is appreciably lower than the provincial average, while the London average cost is no less than 40 per cent lower than the average provincial figure.

Brighton is the only town, according to the author, which has a distinct advantage over the London water companies; this advantage arises from Brighton being situated immediately under the great chalk downs, which form an enormous natural reservoir.

A word or two with regard to failures in London. There was the general breakdown from frost in 1895, and there were the so-called water famines in the East of London in 1895, 1896, and 1898; these comprise all the failures, real and otherwise, in London. In other great towns in England there have been many failures. Manchester has broken down six times since 1874, Liverpool four times, Bradford eight times, while in 1868 Manchester, Sheffield, Bradford, Halifax, Newcastle, and many other towns suffered severely, but London not at all. During the last twenty-five years the eight London water companies have only actually broken down three times between them, while the eight next largest towns have done so at least thirty times; moreover, whenever there is a breakdown in a municipal supply, such as all these great towns enjoy, with the single exception of Bristol, the ratepayers have not only to put up with the inconvenience, but have also to pay for the repairs.

We have no hesitation in saying that there is no water supply in the world which is looked after with such constant and systematic care as that of London. Over 600 samples a month are examined by the companies' chemists; these samples are taken daily from all the filtering stations belonging to the London water companies, and the slightest abnormal condition at any point is immediately communicated to the company concerned by telephone or telegraph. It is by this constant supervision that the very high character of the London water supply is maintained.

Practical Organic Chemistry; the Detection and Properties of some of the more important Organic Compounds. By Samuel Rideal, D.Sc. (Lond.), F.I.C., F.C.S. Second Edition. London: H. K. Lewis. Pp. 172.

The more important tests and reactions of the common organic compounds are collected together in this volume; the most characteristic reactions are distinguished by an asterisk, while a brief summary of the distinctive tests for each group of bodies is also given. As a help to the medical student a list of the *Materia Medica* preparations and organic compounds included in the British Pharmacopœia is also given. In this edition several additional organic substances have been included, as well as a few other compounds of general interest.

The substances dealt with in this volume are the organic acids with the cyanide group; the carbohydrates, including the glucoses, saccharoses, and starches; the organic bases, with the fixed and volatile alkaloids; and neutral substances, such as the alcohols, albumen and gelatin, chloroform, the aldehydes, ethers, &c.

At the end of the book, the order of analyses for the detection and identification of the commoner organic substances is given. The book is well and clearly written, and well adapted for the use of students.

Chemistry for Continuation Schools. By R. L. Taylor. Manchester: Thomas Wyatt. 1899. Pp. 52.

The course of experimental lessons in chemistry contained in these pages was originally intended for teachers in the evening continuation schools of the Manchester School Board; but it has been found to be of great use

when put into the hands of the pupils. The instruction given in this book is essentially elementary, and is intended only for beginners; the descriptions being clear and the experiments simple, we have no doubt but that it will be of great use in the classes for which it is intended.

A Manual of Pharmaceutical Testing for the Man of Business and his Assistants. By Barnard S. Proctor, F.I.C. Second Edition. London: The Chemist and Druggist. 1899. Pp. 192.

The present edition of this book includes various notes which have been accumulated by the author since the appearance of the first edition in 1891, and up to the time of the publication of the British Pharmacopœia for 1898.

Such directions for testing are given as will, it is hoped, enable any ordinary pharmacist to examine and determine the quality of his chemicals with such reagents, &c., usually found at the dispensing counter. The author has endeavoured to point out the probable impurities which may be present, and it is to these the tests specially apply; adulterations are of course more difficult to detect. We must express some surprise at the inclusion of a chapter on manipulation and apparatus, such as weighing and measuring, specific gravity, precipitates, &c. There is far too great a tendency to include such chapters in books of this class, and we are certainly of opinion that every pharmaceutical chemist would have such knowledge at his fingers' ends.

As for the rest of the book, we have no fault whatever to find; it is well written and arranged, and will be a useful addition to the pharmacist's book-shelf.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., Nos. 10, 11, and 12.

These three numbers contain no matter of chemical interest.

Journal de Pharmacie et de Chimie,
Series 6, Vol. ix., No. 7.

This number contains no matter of chemical interest.

No. 8.

Compounds obtained with the Fatty Aldehyds and Mercuric Sulphate.—G. Denigès.—Already noticed.

Method of Testing for, and the Composition of, Oils of Acetone.—A. and P. Buisine.—Oil of acetone obtained from grease contains only traces of dimethylketone, not more than 5 per cent; it contains at least 90 per cent of compounds with an acetonic function, of which 75 per cent are soluble in water. This portion is formed to a very great extent of ethylmethylketone. Comparative tests have been made with samples of oils of acetone from a factory where the acetone was made by means of pyrolignite of lime; these oils are very different in composition, being much poorer in ketones passing over below 90°, they hardly contain half the quantity of ethylmethylketone that the former ones do, while they are much richer in the higher ketones.

No. 9.

Iodised Sulphur and Iodide of Sulphur.—L. Prunier.—Iodised sulphur is prepared by heating sulphur to about 115 to 120°—that is, to just about melting-point—and gradually adding to it an equal quantity of iodine. Stir till the iodine is dissolved and allow to cool; the product crystallises completely in a blackish brown mass—which must be kept in well stoppered flasks, as the iodine is very volatile. When reduced to powder, iodised sulphur immediately gives up its iodine to a solution of hyposulphite. There are several iodides of sulphur: the one experimented on was formed by first heating the sulphur to its second fusing-point; a thermometer is then plunged into the mass, which is allowed to cool down to about 200°, when the pasty state is reached; the coarsely-powdered iodine is then gradually added (4 parts of iodine to 1 of sulphur). The combination takes place with considerable energy. When all the iodine is added, the mass is allowed to cool; it, however, always contains iodised sulphur in varying proportions.

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With a Preface by the Author.

*** *In preparing a second edition of the translation of Meyer's "Outlines of Theoretical Chemistry," the translators have availed themselves of the second edition of the German, published in 1893, a few years before the death of Lothar Meyer. Whilst the original form has been still retained, they have, by occasional footnotes and appendices, sought to bring the book up to date.*

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THE CHEMICAL NEWS.

Vol. LXXX., No. 2081.

SYMBIOSIS.*

By Professor MARSHALL WARD, F.R.S.

Synopsis.

Origin of the idea and of the term. Differences between parasitism and symbiosis.

Lichens, previously regarded as autonomous plants, are shown to be dual organisms, a symbiosis of alga and fungus. Controversy regarding the lichen theory, and establishment of the latter by means of synthetic cultures.

Other cases of symbiosis known previous to 1880. Algæ in the stems of *Gunnera* and the roots of *Cycas*, in the thallus or fronds of *Anthroceras*, and *Blazia*, *Azolla*, *Lemna*, &c.

Extension of the idea of symbiosis: insect fertilisation, epiphytes, &c.

Galls not necessarily due to insects, but may be due to the irritating action of fungi or bacteria. Phytocecidia of the Aleppo pine, &c.

Symbiosis in animals. Green infusoria, hydra, sponges, &c.

Mycorhiza, the roots of many humus plants curiously swollen and modified owing to the presence of fungi, which do not injure the plant, but link its roots to the decomposing leaves around. Explanation as an instance of symbiosis. Evidence partly anatomical and partly experimental.

"Budding" and "grafting" are processes involving the establishment of a symbiosis.

The nodules on the roots of leguminous plants. Discovery and controversy as to their nature. They contain living bacteroids, which penetrate the root hairs and flourish in the living cells. Universality of these nodules on healthy roots. Hellriegel and Willfarth's cultures, and evidence as to the fixation of nitrogen. Laurent and Schloesing's proof that nitrogen is fixed from the air.

The leguminous nodules a case of symbiosis, comparable to galls.

Other instances not yet explained. Nodules on the roots of *Juncus*, *Myrica*, and other plants.

Symbiotic fermentations. All natural fermentations mixed. Pure cultures and the importance of synthetic cultures.

Kephir, the ginger-beer plant, and other instances of symbiotic ferments. Decomposition of cellulose. Nitrifying and denitrifying organisms. The direct alcoholic fermentation of starch by the simultaneous action of two fungi.

Return to the idea of symbiosis. Necessity of limiting the term. Antibiosis (antagonism). Metabiosis. Difficulty of distinguishing in given cases. Hypothetical considerations, and importance of further investigations.

Particular Cases.

The above may be accepted as affording general headings under which the subject of symbiosis might be treated.

For the purposes of this discussion I proceed to consider some special cases, and limit myself—as requested to do—to certain aspects of symbiotic fermentations.

Several cases of symbiosis among bacteria are now known. Apart from numerous instances of temporary association between pathogenic micro-organisms and animals such as earth-worms, rats, flies, ticks, and mosquitoes, and which disseminate their germs and infect cattle, sheep, horses, and men, reminding us of the transference of the spores of *Botrytis* by bees, which carry this parasite with the pollen and infect the stigmas of bilberries with the parasite; or which act the part of intermediate hosts to the disease germs, much as certain pond snails do to the liver-fluke of sheep, we now know several cases of symbiosis between two species of bacteria or of fungi, or between a bacterium and a fungus, each symbiont being incapable of carrying on alone the work which the symbiotic association is able to perform—a point which is essential to the definition of symbiosis in the narrower sense, *i.e.*, the co-operation of two associated organs to their mutual advantage.

A striking example is afforded by certain bacteria concerned in the destruction of cellulose in ponds, bogs, rivers, &c. Van Senus found that a certain anaërobic bacterium, resembling, if not identical with, Van Tieghem's *B. Amylobacter*, though incapable of dissolving cellulose by itself, can do so if associated with another bacterium, also incapable of itself attacking cellulose. *B. Amylobacter* can ferment pectose compounds, and is thus capable of isolating cells one from another, but cellulose is not attacked by it.

Van Senus believed that the one bacillus destroys certain products of fermentation excreted by *B. Amylobacter*, which inhibit its cellulose-fermenting powers.

I may remark here that, if a sound potato, rhizome, or other underground organ is placed in water and the air exhausted as completely as possible, I almost invariably find its cellulose walls destroyed in a few days by a mixture of bacteria, and with the symptoms found in many kinds of "wet rot." There is no reason to believe that these organs would rot if merely wet and not deprived of air, since they lie in ordinary soil—even moist soil—for weeks or months, with plenty of water in their tissues, and respire oxygen, as is well known. The presumption is that the anaërobic conditions set up in the experiment described favour certain forms of soil bacteria, such as Van Senus worked with, and enable them to co-operate in the destruction of the cell walls.

An even more remarkable example is given by Winogradsky, who found that the anaërobic bacterium known as *Clostridium Pasteurianum* is able, if supplied with abundance of dextrose and protected from the access of oxygen, to fix atmospheric nitrogen. In the cultures, and presumably in the soil, the *Clostridium* was found to work when protected by a mantle of aërobic bacteria. In fact, the nitrogen-fixing *Clostridium* was working in the meshes of the oxygen-consuming species, and forming gelatinous flocks like the well-known grains of kephir, or of ginger-beer plant.

Yet another striking instance of symbiotic association has recently been given by Omeliansky. In experiments on nitrification at Bonn, the assertion had been made that the nitrifying organisms—*i.e.*, the bacteria known to oxidise ammonia to nitrous acid, and nitrous acid to nitric acid—could be grown and made to do their specific work in media containing proteids or other organic nitrogenous bodies. Now this was directly contradictory of the experience of Warington, Winogradsky, and other workers, who had found that one great peculiarity of these nitrifying organisms is that they refuse to grow on such media; they are incapable of using organic nitrogen. Several workers then showed that the Bonn observers had inadvertently employed mixtures of two or more species, and Omeliansky undertook a critical investigation of the whole subject, and has put forward the following explanation of the tangle:—

If *Nitrosomonas*—the bacterium which oxidises ammonia to nitrous acid—and *Nitrobacter*—the bacterium which further oxidises nitrous to nitric acid—be sown together or separately on a medium containing organic nitrogen, no growth or change occurs.

But if a bacterium capable of decomposing the organic nitrogenous medium, *e.g.*, *Bacillus ramosus*, is added to

* Read before the British Association (Sections B and K), Dover Meeting, 1899.

the above-mentioned *Nitrosomonas* and *Nitrobacter*, the associated three organisms are able to carry out all the processes and complete the cycle of nitrification. That is to say *B. ramosus* breaks down the gelatin and ammonia is formed; this is then oxidised to nitrous acid by *Nitrosomonas*, and the nitrous acid is further oxidised to nitric acid by the *Nitrobacter*.

If *B. ramosus* and *Nitrosomonas* only are sown together, then only nitrous acid is formed, because the latter organism is only capable of carrying the oxidation the one stage.

If *B. ramosus* and *Nitrobacter* only are used, then only ammonia is formed, because the latter organism cannot oxidise ammonia.

If we try to imagine the working of this association of organisms in the soil, and bear in mind the frequent co-existence and action of the de-nitrifying bacteria which Gayon and Dupetit, Giltay and Aberson, Warington and others, have familiarised us with, a glimpse is obtained of the very complex symbioses which may be concerned in the circulation of nitrogen in Nature. Moreover, some of these de-nitrifying bacilli appear to be anaërobic, and can only work in the surface soil if protected from the access of oxygen—say, by an associated aërobic bacterium.

Another interesting case is the following :—Perdix a few years ago isolated from water an anaërobic bacterium which converts starches into sugars, which with the aid of a yeast can be fermented, the whole process going on in association.

Other cases of symbiotic associations of bacteria exist among the forms concerned in the reductions of sulphates and the oxidation of sulphuretted hydrogen, the iron bacteria, &c.; but I propose to mention only one or two further examples, taken from the true fungi.

Symbiotic associations of fungi are probably common, but only a few cases are as yet established, and these principally among the ferment-fungi.

Van Laer has called attention to the symbiotic co-existence of two yeasts in many beers, explaining certain peculiar after-fermentations as due to the action of one yeast acting on the medium improved for it by the other.

The Japanese have long been in the habit of brewing a peculiar fermented liquor known as rice-wine, or saké. Rice grains are steamed, and when cool are infected with a mould fungus now known as *Aspergillus Oryzæ*. When the rice is quite mouldy, at which time it emits a peculiar odour like that of pine-apples, the starch is found to be rapidly turning to sugar, under the action of a diastatic enzyme secreted by the fungus.

This decomposing rice is then placed in water and exposed to the action of a yeast, which rapidly ferments the sugar, and the alcoholic saké results.

So closely is the yeast associated with the *Aspergillus*, that, in practice, the alcoholic fermentation commences soon after the enzyme of the *Aspergillus* begins to hydrolyse the starch of the rice, and for some time a controversy existed as to whether the yeast was not really part of the life-history of the *Aspergillus*. Several observers have now shown, however, that we have here a striking case of symbiosis.

On reviewing these examples, we shall find that very different degrees of association of the organisms are to be met with.

At the one end of the series we find two organisms merely associated for a short time, *e.g.*, bacilli and worms, bees and botrytis-spores, and, so far as we may speak of symbiosis at all in these cases, it is merely temporary or disjunctive.

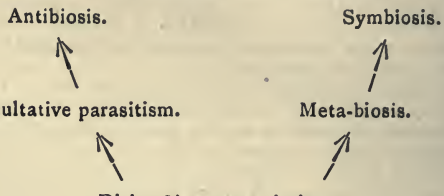
At the other end of the series we have a close permanent combination of the two organisms working in unison, *e.g.*, the lichens and Winogradsky's *Clostérium* with its protective mantle of aërobic bacteria; also the ginger-beer plant and kephir.

But between these extremes it is possible to find all stages, the half-way house being met with in cases such as the saké ferment, where the *Aspergillus* evidently prepares the way for the *Yeast*.

It has been proposed to apply the term *Metabiosis* to such cases.

It must not be forgotten that there are extremes in the other direction, where one of the two associated organisms is injuring the other, as exemplified by many parasites, but these cases I leave out of account here. This state of affairs has been termed *Antibiosis*.

It seems not impossible that the biological relationships of these cases one to another could be shown thus:—



The Physiology of Symbiosis.

It will be an interesting exercise to see if we can get any further glimpses into the physiology of the phenomenon of Symbiosis.

When we come to enquire as to the processes which lead to enhancement of the functional activity of one organism by another living symbiotically with it, the matter presents many difficultes; for it is at the outset quite obvious that many things are possible, and soon becomes evident that a tangle of complexities lies before us, as always in the inter-relations between associated biological units. We need go no further than the examination of the possibilities in the inter-relations between a weed and a cultivated plant, or between two trees in a forest, for illustrations of this truth.

Confining attention for the moment to closely associated symbionts, such as those composing a lichen, the ginger-beer plant, or a clump of symbiotic bacteria or fungi, researches have made it practically certain that the provision of definite food-materials by the one symbiont for the other may be an important factor; *e.g.*, an alga supplies a fungus with carbo-hydrates, or a fungus converts starch into the fermentable sugars which the associated yeast needs. In other cases the advantage derived is one of protection from some injurious agent—*e.g.*, the aërobic bacterium prevents the access of oxygen to the anaërobic one. But there is evidence which suggests that mere nutrition or protection is not the only, or even the principal, factor involved. It is well known that the products of fermentative actions are frequently poisons, and we all know of cases where such poisonous excreta of living cells act as stimuli to other living cells, if supplied to them in minimal doses and very gradually: I need only instance the effects of tobacco or alcohol on man, in illustration of this.

Several observers have shown that in presence of a particular food-substance the living cell is stimulated to produce and excrete a particular enzyme, while the substitution of another food stimulates the organism to excrete a totally different enzyme.

Now let us see if there is any evidence to support the hypothesis that some such stimulative action is exerted by one symbiont on another. To a certain extent we find such in the remarkable vigour and large size of the algal cells in a lichen as compared with the same cells living an independent life, and in the persistent zone of brilliant green and often hypertrophied cells of leaves in which certain fungi are living, the gigantic cells of the nodules on leguminous roots in which the bacteroids are living, and many other cases; but since it is impossible to say how far these are cases of merely enhanced nutrition, we will pass them by and seek for other instances.

One of the earliest I can find is Hugo Schulz's demon-

stration, in 1888, that minute quantities of poisons—such as corrosive sublimate, iodine, iodide of potassium, bromine, arsenious acid, chromic acid, sodium salicylate, or formic acid—when added to yeast in 10 per cent grape-sugar solution, immediately raise the fermentative activity of the organism, as measured by the amount of carbon-dioxide evolved. Effront, in 1894, showed that hydrofluoric acid acts similarly on yeasts, butyric ferments, and *mycoderma*, and, later, that the same is true of formaldehyde, salicylic acid, picric acid, &c.

What looks like another case in point is Johannsen's results of experiments with seeds, buds, &c., treated with ether or chloroform; respiration is increased, and the whole course of metabolism so altered that in some cases buds of flowers can be stimulated to open long before their normal period.

The results obtained by Farmer and Waller with carbon-dioxide, which was found to induce an initial acceleration of the movement of the protoplasm in *Elodea*, may be a further instance.

Pfeffer has recently called attention to a still more remarkable instance—that it is possible, by etherising the living cells of *Spirogyra* to alter the type of nuclear division from *mitotic* (indirect) to *a-mitotic* (direct). Massart had shown that callus, the hypertrophied tissue developed under stimulation by mites, fungi, exposure to air, &c., is formed of cells which divide with *a-mitotic* nuclear division; and other cases occur. But it is even more to the point for my purpose that Gerassimoff, in Pfeffer's laboratory, found *Spirogyra* driven to *a-mitotic* division by associated bacteria and other organisms, which he regards as a case of symbiosis.

Now it may be regarded as certain that if a cell can be thus stimulated to alter the details of so fundamental and complex a morphological process as its cell-division by the action of associated organisms, the metabolic activities of its protoplasm are being driven into very different channels from the normal, and many physiological processes must be affected.

Of course I am here raising questions which concern the border-line between health and disease, and much investigation is still required as to the meaning of these matters; but I ought to add that, according to Pfeffer, the etherised cells can be again restored to their normal state if the traces of anæsthetic are washed out, and those familiar with Kleb's experiments on other algæ will appreciate the significance of this one with *Spirogyra*.

However feeble the evidence may be, we can at least say, then, that there is some evidence in support of the hypothesis that one symbiont may stimulate another by excreting some body which acts as an exciting drug to the latter—just as truly as certain drugs act as stimulants to some cell or organ of a higher animal, and no doubt in a fundamentally similar manner. It will be noted that such drugs are frequently excreta from vegetable cells.

But there is another—perhaps more indirect—way in which one symbiont may enhance the activity of another. It has long been known that the accumulation of the products of metabolism of a cell tend to inhibit the activity of that cell, and that if by any means we can destroy or remove the metabolite as it is formed, the cell concerned can go on working. Similarly with ferments, and even with enzymes, the accumulation of the products gradually inhibits the action, as Tammann showed in the case of amygdalin and emulsin, and Brown and Morris and Lea in the case of starch and diastase, to mention two illustrations only.

Now suppose we have two organisms, A and B, living in symbiosis, and suppose that A is capable of hydrolysing starch by the excretion of diastase, while B removes the product of hydrolysis, by fermenting the sugar as fast as it is formed; in this case there is every reason to expect that A will complete its hydrolysing action to the utmost, not only because it is of advantage to A to be relieved of the inhibiting sugar, but because the diminution of the sugar reacts as a stimulus to the secretion of more enzyme.

There is yet another point to be considered. Katz, in 1898, published some results confirming in many points the discoveries of Wortmann, Brown and Morris, and others, that fungi, bacteria, embryos, and other enzyme secreting organisms, not only vary the extent and kind of enzyme secreted, but can be stimulated to vary the enzyme according to the quantity or quality of food materials at hand.

I think this line of enquiry may lead to results in the present connection, as it is obvious that the products of fermentation of an organism A must be favourable, or without effect, or deleterious to the action of another, B, in its immediate neighbourhood. Moreover, it is shown that a product which is, *per se*, devoid of either favourable or deleterious action, may acquire one or the other if the concentration increases.

Katz regards the action of sugars as not a purely chemical one, but as a physiological stimulus; and without pretending to understand the distinction in detail, we may admit the importance of the experimental facts, and not only seek for, but also hope for, more light.

Here, then, is a brief sketch of some of the salient features of symbiosis, and of some of the physiological factors concerned in the processes; and though it is far from exhaustive, it may serve our purpose to-day of starting a discussion, and of showing some lines along which further investigation is desirable.

SYMBIOTIC FERMENTATION: ITS CHEMICAL ASPECTS.*

By Professor HENRY E. ARMSTRONG, F.R.S.

1. It is open to question whether the establishment of symbiotic relationships involves more than a subdivision of labour—whether the associated organisms combine in carrying the chemical change through any one phase.

2. There is an absence of positive evidence tending to show that the one member of a pair of symbiotic organisms or agents does more than prepare the way for the other by effecting a change which the second is incapable of inducing, leaving it to the second to carry on changes in which the initiating organism plays no part. A rough parallel to the case here contemplated would be that afforded by the occurrence of lactic followed by butyric fermentation under the influence of distinct organisms. These are strictly independent and sequent phenomena, the one change apparently setting in only when the other is complete.

3. In symbiotic fermentation, however, the two sets of changes seem at least to run parallel.

4. It may be a function of the one organism to remove from the sphere of action, as it arises, a product which would tend either to inhibit the change by which it is formed or to promote its reversal.

5. Or the one organism may produce a change which, although minute, is sufficient to place the companion organism under the most favourable conditions. For example, a minute proportion of acid favours the hydrolysis of cane-sugar by invertase. Hence it may be supposed that in a neutral or faintly alkaline solution yeast would ferment sugar only slowly, if at all, whilst if associated with an organism capable of producing, say, a minute proportion of lactic acid it would act rapidly. A case apparently of symbiosis, which possibly comes within this definition, is that referred to by Marshall Ward as studied by Van Senus.

6. Or, again, the one organism may become associated with the hydrolyte, and thus shield or mask a particular "centre" in it, thereby making it possible for the second

* Read before the British Association (Sections B and K), Dover Meeting, 1899.

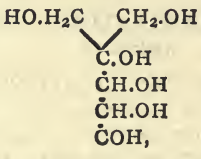
organism to actively affect the molecules at other centres. This case corresponds to the removal of a ward from a lock, and the consequent possibility of using a simpler key. What is in some cases a more nearly exact parallel is afforded by the production of glycuronic acid by the oxidation of the compound of glucose with chloral: in glucose, the COH centre is super-attractive to most oxidising agents, but when this centre is masked the attack is transferred to the opposite $CH_2(OH)$ group.

7. Another case is considered subsequently (§ ii.).

8. Fermentation is certainly at bottom a process of *hydrocatalysis*, and it can scarcely be doubted that the function of the enzyme is to introduce water into the circuit of change—in fact, to establish a circuit in which hydrolytic changes can occur, although not of the ordinary kind, but reductive on the one hand and oxidative on the other.

9. Hence we may speak of the substance fermented as the *hydrolyte*, of the ferment as the *hydrolyst*, and of the products of hydrolysis as the *hydroschists*.

10. It is more than probable that the products ordinarily obtained are but end products of a series of changes, and that only some of these are enzymic, whilst others occur, as it were, naturally, and are partly analytic and partly synthetic in character. Thus, in the formation of the inactive amyl alcohol in fusel oil, it may be supposed that glucose is resolved by *fermentation* into a mixture of glyceraldose and glyceroketose, which spontaneously interact forming a new hexose,—



and that this in turn becomes *fermented* to isobutylcarbinol, &c. It is not even known whether fusel oil is a product of fermentation by pure yeast; still less, therefore, can it be decided whether the two successive fermentations here contemplated are the acts of one organism, or of organisms which are in any sense symbiotic. But it seems almost certain that one and the same organism can produce a variety of changes.

11. It is conceivable that two symbiotic organisms may so act that the one produces a substance A, the other a substance B, and that these products interact, forming a third substance; and that the two organisms attack either one and the same substance, or different substances. In such a case the fermentation would be different from that produced by either organism singly. Such would be a case of truest symbiosis.

12. The conversion of lactic into butyric acid, of glycerol into butanol, and the formation of fat are certainly cases of fermentations in which synthetic changes occur, and it may well be apart from enzymic action.

13. There is little doubt that the importance of the part played by synthetic changes in fermentations, especially in the case of nitrogenous compounds, is at present far from being appreciated.

14. But however many steps may be involved in some fermentations, at least the attack on several centres must be simultaneous, and must occur in one and the same circuit, as the change involves expenditure of energy at some centres, and this must be supplied from those others at which energy is developed. A complex carbohydrate molecule undergoing fermentation may, in fact, be compared with a series of voltaic cells of unequal electromotive force in series. It is difficult in any other way to account for the re-solution of a single molecule into so many others, such as occurs, for example, in ordinary alcoholic fermentation.

15. Such simultaneous attack is possible, probably because the enzyme is so constituted that it can attach itself at several points along the chain; the hydrolyte, in fact, is comparable with a complex lock, the hydrolyst with a complex key. It is possible thus to picture contact as being established between several more or less distant centres in a complex molecule, and a "ripple of change" as pervading the system in consequence. Enzymes with restricted powers, such as invertase and diastase, probably can attach themselves only to a single centre, and their action is directly and simply hydrolytic.

16. In some cases, such as the formation of fat, it would seem necessary to suppose that several molecules may become associated together through the agency of the hydrolyst, so that reductive processes may go on almost entirely in the one set; whilst in another corresponding oxidative processes take place, which furnish the energy required to effect the reduction. On the other hand, it is conceivable that oxygen directly intervenes in the formation of fat, and that the process is not merely one of hydrocatalysis.

17. That no very complex mechanism is needed to produce effects such as are believed to be involved in fermentations, follows from the fact that dextrose, for example, may be resolved into lactic acid by digestion with alkali and levulose into levulinic acid, $CH_3.CO.CH_2.CH_2.COOH$, by heating it with an acid, the latter being an especially remarkable case.

18. If the phenomena are as suggested, it does not seem probable that true symbiotic fermentation is likely to occur as a consequence of the simultaneous attack of a single molecule by several organisms; rather is it probable that associated molecules undergo change under the influence of a single organism or agent which determines their association. And hitherto apparently no case has been met with in which a substance has been observed to give way to a pair of organisms, neither of which can attack it singly.

19. The assimilation of nitrogen by plants, which is believed to take place in the symbiotic growths found on the roots of the Leguminosæ, is a phenomenon of which at present no explanation can be given, as this element cannot enter into combination with either hydrogen or oxygen unassisted; its absorption must take place in a circuit in which changes occur from which the necessary energy may be derived. As hydrogen is liberated in many fermentations, it appears not improbable that nitrogen may be brought into circuit by acting as a hydrogen depolariser; one function of the nodule may be to supply carbohydrate, which is fermented by the bacteroid in circuit with the nitrogen.

20. Symbiosis, as distinguished from parasitism, involves the conception not only of the concurrent existence of organisms, but of their useful concurrency; indeed, any other form of symbiosis is difficult to imagine, and *antibiosis* is a contradiction in terms. It is desirable that we should remain satisfied with the term until our knowledge of the actual character of the changes involved in ordinary as well as in symbiotic fermentations is far greater than is now the case; at present it is impossible to draw valid distinctions.

Note.—The explanation of fermentation adopted in this note is given in my Address to the Chemical Society in 1895 (*Trans.*, p. 1136). Green, in his recent work on Enzymes, speaks of Baeyer having put forward, in 1870, the hypothesis that fermentation is due to electric hydrolysis. This is incorrect. Baeyer's paper is entitled "Ueber die Wasserentziehung und ihre Bedeutung für das Pflanzenleben," &c. He makes no reference whatever to the manner in which water might be withdrawn, but merely shows that the withdrawal of water and the subsequent addition of its elements in a different order would produce effects such as are observed in fermentations.

CONDENSATION OF GLYCOLLIC ALDEHYDE.*

By HENRY J. HORSTMAN FENTON, M.A., F.R.S.,
and
HENRY JACKSON, B.A., B.Sc.

IT has been pointed out by one of the authors in previous communications that tartaric acid when oxidised in presence of a small quantity of ferrous iron, gives rise to dioxymaleic acid, $C_4H_4O_6$; and that this acid readily decomposes in aqueous solution, giving glycollic aldehyde, $C_2H_4O_2$. This aldehyde has recently been isolated by the present authors in a crystalline state (*J. C. S. Trans.*, 1899, p. 575). It was further shown (Fenton, *Ibid.*, 1897, p. 375) that glycollic aldehyde, when heated to 100—105° under reduced pressure, undergoes polymerisation, giving rise to a true hexose, $C_6H_{12}O_6$. The condensation effected in this way is not complete, and the resulting product has to be purified from the unaltered glycollic aldehyde by treatment with absolute alcohol; the yield of the sugar is consequently small, so that further study of its nature was extremely difficult.

The authors have therefore sought to modify the method of production with a view to increasing the yield, and have studied the results of effecting the condensation (1) at higher temperatures; (2) under the influence of alkalis.

If the aldehyde be heated to about 130—140° for a short time a substance is obtained which dissolves easily in water, but is precipitated as a brownish white powder on addition of alcohol; whereas at a temperature of about 160—170° a brown spongy substance is formed, which is nearly insoluble in boiling water, and on analysis its composition is found to be approximately $C_6H_{10}O_5$.

When an aqueous solution of the aldehyde is mixed with a dilute (1 per cent) solution of caustic soda, it begins to turn brown almost immediately. After standing for about twenty-four hours at the ordinary temperature (about 15°) the mixture no longer reduces Fehling's solution in the cold, nor answers Schiff's aldehyde reaction with magenta. The solution now gives with phenylhydrazin a precipitate consisting of clusters of bright yellow needles, which melt at 158° and have the composition of a hexosazone, $C_{18}H_{22}N_4O_4$. The pure osazone is very soluble in ethylacetate, sparingly soluble in ether, benzene, and boiling water. The crystalline form, melting-point, and behaviour towards solvents appear definitely to establish its identity with β-acrosazone, which was obtained by Fischer and Tafel from the condensation-product of "glycerose" by alkalis.

When calcium hydroxide is employed in place of caustic soda, an exactly similar result is obtained. After removing the calcium from the solution by exact precipitation with oxalic acid and evaporating to small bulk at 40° under diminished pressure, it was dissolved in alcohol, filtered, and then precipitated with ether. The sugar was thus obtained in the form of white flocks which aggregate to a pasty solid on standing in a vacuum.

The properties and configuration of β-acrose have not hitherto been studied, owing to the fact that it could not be obtained in quantity unaccompanied by other sugars; the authors hope, however, by the present method of preparation to obtain the sugar in quantity sufficient for a more complete study.

The formation of a true hexose, and a substance resembling starch and cellulose, from glycollic aldehyde, is of especial interest from its bearing on carbohydrate formation in plants. The remarkable part which a small quantity of ferrous *iron* plays as a carrier of *atmospheric oxygen* in presence of direct *sunlight* has already been pointed out (Fenton, *Brit. Assoc. Report*, 1895; Fenton and Jackson, *Trans. Chem. Soc.*, 1899, 1): in the absence of any of these three conditions, the oxidation does not take place. In plant metabolism these conditions coexist; this reaction may not only throw light upon the function of small quantities of iron existing in chlorophyll, but may explain the conversion of tartaric acid, which is so common in unripe fruits, to the sugars of the mature fruit.

*Read before the British Association (Section B), Dover Meeting, 1899.

THE ACTION OF IODIDE OF POTASSIUM IN SOLUTION ON MERCUROUS IODIDE.

By MAURICE FRANCOIS.

I HAVE already shown that mercurous iodide is easily decomposed into mercury and dissolved mercuric iodide under the influence of a certain number of liquids, and that these reversible decompositions obey the laws of the dissociation of salts by water. To conclude this subject I will describe, as obeying the same laws, the action of solutions of iodide of potassium on mercurous iodide.

We know that iodide of potassium decomposes mercurous iodide into mercury which is deposited, and mercuric iodide which goes into solution. The following are the facts which I observed when operating at a constant temperature of 20°, and acting on mercurous iodide with a normal solution of pure iodide of potassium (166 grms. per litre).

Complete Decomposition.—The decomposition is complete when the iodide of potassium is used in large quantity—for example, if we agitate 2 grms. of mercuric iodide with 20 c.c. of the normal solution of iodide of potassium. The insoluble portion is formed entirely of small globules of mercury.

Incomplete Decomposition.—If the quantity of mercurous iodide is more considerable, a portion only is decomposed. The insoluble portion is a greenish-yellow powder, formed of a mixture of mercurous iodide and finely divided mercury. This is what happens when, for instance, we agitate 20 c.c. of the normal solution of iodide of potassium with 6·54 grms. of mercurous iodide. The actual proportions used are those corresponding to the following equation:—

$$\underset{654}{Hg_2I_2} + 2KI = \underset{232}{HgI_2.2KI} + Hg,$$

by which is represented generally the action of iodide of potassium on mercurous iodide. The action is thus limited. Whatever may be the proportions used, when the decomposition stops and equilibrium is reached, 100 grms. of the supernatant liquid contains 11·9 grms. of mercuric iodide in solution at a temperature of 20°.

Inverse Action. — If we saturate a certain quantity of the normal solution of iodide of potassium at 20° with mercuric iodide, this solution—when placed in contact with metallic mercury—attacks it in the cold and mercurous iodide is formed in abundance. But this inverse formation of mercurous iodide stops of itself when a large proportion of mercurous iodide is present in the solution.

For the temperature of 20° we find that, at the moment when equilibrium is established, 100 grms. of the liquid contains 11·9 grms. of mercurous iodide in solution—a figure already found in the experiment on decomposition.

We have used the normal solution of iodide of potassium, but it is evident that these facts will equally apply to solutions of different concentration. Nessler's reagent attacks metallic mercury very energetically, giving mercurous iodide. The preceding determinations were made in the following manner:—For the limited decomposition we left 200 c.c. of the normal solution of iodide of potassium and 65·4 grms. of mercurous iodide in contact for twenty-four hours, in an oven kept at 20°, with constant stirring. At the end of this time we take 5 c.c. of the clear supernatant liquid and determine its weight, and estimate the mercury and the iodine by electrolysis.

To make the same determination in the inverse action we left 100 c.c. of the normal solution of iodide of potassium saturated with mercuric iodide and 200 grms.

of mercury in contact for twenty-four hours, with frequent stirring. At the end of this time we took, as above, 5 c.c. of the clear liquid for the estimation, after weighing, of the mercury and the iodine.—*Journ. de Pharm. et de Chim.*, Series 6, vol. x., No. 1,

VOLUMETRIC ESTIMATION OF PHOSPHORIC ACID IN PHOSPHATES.

By Dr. SIGISMUND LITTMANN.

THE numerous experiments that have been made of late years for the purpose of obtaining a rapid and practical method for the estimation of phosphoric acid in phosphates, shows very clearly that all the usual methods employed, even those using citrate, are too long and inconvenient.

In what follows I propose to explain a new method, very easy of execution, of which the results are rigorously exact, and which fulfils all the requirements of practical chemists, as will be seen from the subjoined analyses.

The manner in which orthophosphoric acid behaves with alkalis and various indicators is known, but perhaps not sufficiently appreciated. I may mention that, in my opinion, the best indicators are methyl-orange and phenolphthalein.

The salts of orthophosphoric acid give alkaline and not neutral reactions with these bodies; the reactions of the monohydrodimetallic phosphates, and of the dihydromonometallic phosphates with methyl-orange are alkaline, and with phenolphthalein they are acid, while with the free acid, H_3PO_4, the reactions are acid with both bodies. The usual method for determining the acidity of phosphoric acid is founded on this manner of behaving. Although well known it is as well to draw attention to the successive saturation by means of equations. Starting from free H_3PO_4 we obtain, after having added methyl-orange until the yellow colouration titrates with caustic soda, monophosphate of soda.

$$\text{I. } H_3PO_4+NaOH=NaH_2PO_4+H_2O.$$

After the addition of phenolphthalein until a red colouration appears, on adding NaOH we obtain diphosphate of sodium—

$$\text{II. } NaH_2PO_4+NaOH=Na_2HPO_4+H_2O;$$

the red colouration taking place at the moment of the formation of the normal triphosphate,—

$$\text{III. } Na_2HPO_4+NaOH=Na_3PO_4+H_2O.$$

In this manner orthophosphoric acid may be easily determined in the presence of other acids, provided that the acids which may be present are modified by the first saturation (I.); H_3PO_4 is only transformed into NaH_2PO_4, which is estimated after the second saturation, by means of phenolphthalein.

The objection which has been made to this method—above all, when using one-tenth normal soda—that the reading is not sufficiently sharp considering that the transformation of NaH_2PO_4 into Na_2HPO_4 corresponds to the state called "amphotere," is not altogether unfounded, but the errors arising from this imperfection may be reduced to a minimum, as is shown by the following analyses.

A certain number of mixtures of HCl, H_2SO_4, HNO_3, and H_3PO_4 in varying quantities (the H_3PO_4 was obtained from a solution of P_2O_5 boiled for some time with HNO_3, until the metaphosphoric acid is completely transformed) were titrated with one-tenth normal soda; the phosphoric acid in each mixture was also determined gravimetrically with molybdate of ammonia.

P_2O_5 per cent.		
Gravimetric results.	By titration.	Difference.
2·30	2·26	0·04
3·84	3·80	0·04
5·78	5·72	0·06
11·33	11·08	0·25
11·47	11·39	0·08
14·49	14·31	0·18
21·87	21·78	0·09

From the results obtained by titration it appears that a proportion of 0·016 per cent was obtained.

Our object is now to make use of this behaviour of orthophosphoric acid for phosphates. The titration with caustic soda gives useless results, as was foreseen in view of the diversity of the bases with which the H_3PO_4 is united and their precipitation by the alkali. It became necessary to transform the monophosphate of calcium and the other phosphates (Mg, Al, Fe) into phosphates of the alkali, and prevent the precipitation of the bases.

R. J. Thomson's method (precipitation by oxalate of soda or ammonium) represents an experiment of this character.

This method, which will not do with phosphates containing iron, is very little used in practice.

For effecting this transformation I use an alkaline citrate; in the course of my experiments, I found that citrate of sodium gave better results than the corresponding salts of potash and ammonium.

It is essential for the citrate to be absolutely neutral. As to its preparation, it is as well to follow the subjoined method:—A pure solution of NaOH (30 grms. of NaOH in 120 c.c. of water) is neutralised, after having added phenolphthalein, with concentrated citric acid, then after twenty-four hours the liquid is filtered so as to separate any precipitate which may have formed; if necessary, it is neutralised a second time and then diluted to 120 c.c.

This solution will keep for a considerable time in well stoppered bottles; it is always as well to test its neutrality before using it. Further, the one-tenth normal solution of NaOH should not contain carbonic acid, and should not be contaminated with either $Ca(OH)_2$ or $Ba(OH)_2$. For the purpose of analysis 10 grms. of phosphate are dissolved in 400 c.c. of water in a flask of 500 c.c. capacity. After having shaken for about half an hour, the flask is filled up to the mark; filter, and use 50 c.c., equivalent to 1 grm., for the titration; add methyl-orange, titrate until there is a distinct yellow colouration, and note the quantity of one-tenth normal NaOH which has been used.

Besides the $CaH_4(PO_4)_2$, we have still NaH_2PO_4 produced from the H_3PO_4. The first body is transformed into NaH_2PO_4 by the addition of 10 c.c. of the citrate solution, $Na_2C_6H_6O_7+CaH(PO_4)_2=CaC_6H_6O_7+2NaH_2PO_4$.

The solution is generally of a greenish colour, owing to the presence of citrate of iron; this considerably facilitates the observation of the change of colour after the addition of phenolphthalein. The titration should be continued to a red colouration; this operation requires very great care.

The titration is finished slightly before the faint red colouration which is caused by the Na_3PO_4 appears. After a few trials we can easily detect the end of the reaction by adding soda until the red colouration is distinct (working on a sheet of white paper) and titrating back with one-tenth normal H_2SO_4 until the colouration disappears.

During this second saturation the solution remains clear; this is a very great advantage over other analogous methods.

The neutralisation may be represented by the following equation:—

$$2NaH_2PO_4+2NaOH=2Na_2HPO_4+2H_2O.$$

We obtain the content per cent of P_2O_5 by multiplying the cubic centimetres of soda used in the operation by 0·71.

Gravimetric results.	By titration.			Difference.
		One-tenth normal		
$Mg_2P_2O_7$.	P_2O_5.	NaOH.	P_2O_5.	P_2O_5.
	Per cent.	C.c.	Per cent.	Per cent.
		Florida Phosphate.		
0·2757	17·65	24·7	17·54	−0·11
0·2722	17·42	24·8	17·61	+0·19
0·2844	18·20	25·7	18·24	+0·44
0·2706	17·32	24·9	17·68	+0·36
0·2809	17·98	25·3	17·96	−0·02
0·2672	17·10	24·5	17·39	+0·29
0·2695	17·25	24·3	17·25	0·00
0·2608	16·69	23·8	16·89	+0·20
0·2813	18·00	25·6	18·18	+0·18
0·2766	17·71	25·0	17·75	+0·04
0·2800	17·92	24·9	17·70	−0·22
0·2772	17·74	25·0	17·75	+0·01
0·2826	18·08	25·6	18·17	+0·09
0·2768	17·72	24·8	17·61	−0·11
0·2758	17·65	25·0	17·75	+0·10
		Bone-ash.		
0·2965	18·98	26·4	18·74	−0·24
0·2669	17·08	24·3	17·23	+0·15
0·2667	17·07	24·1	17·11	+0·04
0·2983	19·09	26·6	18·99	−0·20
0·2728	17·39	24·4	17·32	−0·07
0·2834	18·14	25·4	18·03	−0·11
0·3005	19·23	27·3	19·38	+0·15
0·2820	18·05	25·2	17·89	−0·16
0·3008	19·25	27·3	19·38	+0·13
0·2518	16·11	23·0	16·33	+0·22
		Algerian Phosphates.		
0·2505	16·03	22·7	16·11	+0·08
0·2610	16·70	23·6	16·76	+0·06
0·2442	15·63	21·8	15·48	+0·15
0·2605	16·67	23·5	16·68	+0·01
0·2472	15·82	22·4	15·90	+0·08
0·2323	14·87	20·8	14·78	−0·09
0·2520	16·32	23·5	16·68	+0·36
0·2405	15·39	21·8	15·47	+0·08
0·2580	16·51	23·5	16·68	+0·17
0·2252	14·41	20·3	14·41	0·00
0·2505	16·03	22·6	16·05	+0·02
0·2453	15·70	22·7	16·18	+0·41
0·2452	15·69	22·5	15·97	+0·28
0·2497	15·98	22·4	15·90	−0·08
0·2460	15·74	22·2	15·76	+0·02
		Special Manure.		
0·1019	6·52	9·1	6·46	−0·06
0·1606	10·28	14·6	10·36	+0·08
0·2472	15·82	22·1	15·70	−0·12
0·2353	15·06	20·7	14·77	−0·29
0·2100	13·44	19·0	13·49	+0·05
0·2062	13·19	18·4	13·06	−0·13
0·1426	9·12	12·7	9·02	−0·10
0·1876	11·98	17·1	12·14	+0·16
0·1540	9·85	13·8	9·80	−0·05
0·1224	7·86	11·1	7·99	+0·13

There are some phosphates—especially those which contain much iron or alumina—with which the change of colour of the methyl-orange from red to yellow is not sufficiently distinct, the salts of iron and alumina themselves having an acid reaction.

The change becomes more distinct by diluting the 50 c.c. five times; for such a titration it is necessary to then take 50 c.c. of that solution, add to it 10 c.c. of the solution of citrate without previously diluting, add the phenolphthalein, and complete the titration. The quantity of soda used in the first place is deducted.

It is, as a rule, of advantage to proceed in this manner, the yellow colouration of the methyl-orange being thus eliminated. It is evident that this method enables us to estimate the total phosphoric acid, and not only the phosphates soluble in water; however, in the presence of large quantities of acids the work becomes less easy and the results not so correct. The meta- and pyrophosphoric acids cannot be estimated in this manner.

I have attempted to use a few other indicators, such as litmus, cochineal, tropeoline, curcuma, &c., but without success.

Each analysis—comprising half an hour for extraction and shaking up the solution—lasts only three-quarters of an hour; the double titration, with the necessary calculations, hardly requires five minutes.

I have been using this method for about a year for the analysis of Florida and Algerian phosphates and bone-ashes, as well as for several special manures containing sulphates of potash and ammonium.

The comparative gravimetric method which I used was the citrate method; the one which I have just mentioned might, however, replace it. In some cases, where there were large differences (a maximum of 0·4 per cent), I used the molybdate method, with which I obtained results more in accord with those obtained by titration. The difference with regard to the gravimetric method (citrate) is about 0·13 per cent.

Its exactness and its easy manipulation cause me to believe that this process, in spite of the large number of methods already proposed, will be welcomed by those chemists whom it most concerns.—*Chemiker Zeitung*, xx., No. 68.

ANALYTICAL METHODS FOR DISTINGUISHING BETWEEN NITROGEN OF PROTEIDS AND NITROGEN OF SIMPLER AMIDES OR AMIDO-ACIDS.

By J. W. MALLET,
Professor of Chemistry, University of Virginia.

(Concluded from p. 171).

Behaviour with Cupric Hydroxide (Stutzer's Reagent).

THE formation of insoluble compounds of the proteids with cupric hydroxide, while leaving the simpler amides soluble in the presence of an excess of this reagent, has been extensively adopted as the means of separation, but experiments made in this way have not given the writer much confidence in the method as a general one. In some cases, working with a proteid alone, the copper compound underwent partial solution, a blue liquid being formed, although care had been taken to avoid the presence of free alkali. Possibly this result was due to incipient decomposition of the proteid material. As Stutzer himself has pointed out, peptones are very incompletely precipitated by cupric hydroxide. A further objection is to be found in the very slight solubility of the copper salts of some of the simpler amido-acids, especially leucin and glutamic acid; in a less degree the same statement applies to aspartic acid. Even at the temperature of boiling water the copper compounds of these substances are but very sparingly soluble, and if the liquid after digestion with cupric hydroxide be filtered cold,* the compounds in question will, if present, be almost certainly left on the filter along with the proteid material.

Relations to Alcohol as a Solvent.

It has been repeatedly proposed to use strong alcohol for the precipitation of the proteids, with a view to their quantitative determination, and this even in cases involving the simultaneous presence of some of the amidic com-

* As directed by the Association of Official Agricultural Chemists, Bulletin No. 46 of the U.S. Department of Agriculture, Division of Chemistry (1895), p. 25.

pounds under discussion, such as the flesh bases (See Watts's "Dictionary of Chemistry," revised edition, vol. iv., p. 330, and H. W. Wiley's "Principles and Practice of Agricultural Analysis," vol. iii., p. 453). But not only do the character and amount of the proteids so precipitated or left insoluble vary with the strength of the alcohol and the quantity of it used, but the further serious objection presents itself, that nearly all the simpler amides and amido acids are either insoluble in alcohol or so slightly soluble that it is practically impossible to wash them out satisfactorily from the precipitated or coagulated proteids. A method which is not properly applicable to such important substances as asparagin among vegetable ood materials, and kreatin among those of animal origin, manifestly deserves but little consideration.

Behaviour with several New or Little-used Reagents.

A number of miscellaneous experiments were tried with reagents which have either been but occasionally applied to materials of the kind under examination, or have not been so applied at all, so far as published records show.

A weak solution of pure phenol (carbolic acid), trichloracetic acid, formic aldehyde in aqueous solution, and hydrazoic acid (azoimide) were thus tried, but from none of these reagents were results obtained which furnished any ground for a general method of distinguishing the two classes of nitrogenous materials which were being studied.

Behaviour with Phospho-tungstic Acid.

This reagent, the discussion of which I have left to the last, has proved of much more value than any other I have tried, and its application under proper conditions affords, I believe, a fairly satisfactory practical solution of the question I have undertaken to examine. The use of phospho-tungstic acid for the precipitation in general of nitrogenous compounds, alkaloidal, amidic, and proteid, is, of course, well known and often practised; but some of the special facts on which may be founded its application to the purpose now under discussion are believed to be new, and the particular use made of these points of behaviour has not been before described. In connection with the experiments made with phospho-tungstic acid, the results obtainable from a parallel series of experiments with a strong solution of tannic acid were compared, one of these two reagents being found under special circumstances to replace the other with advantage.

The precipitant was employed not as a sodium or other salt, but as the phospho-duodeci-tungstic acid, crystallised in small cubes and dissolved in dilute hydrochloric acid, 25 grms. of real HCl to the litre. Solutions of 2 degrees of strength were prepared, the one containing 50 grms. of the solid reagent to the litre, the other 100 grms. In the experiments with tannic acid, solutions in like manner containing 50 and 100 grms., respectively, of a remarkably good sample of the reagent, dissolving readily to a perfectly clear liquid, were made use of.

It has been assumed by Stutzer and others that the proteid and allied substances are precipitated by phospho-tungstic acid, while the simpler amides and amido acids are not so precipitated. As qualifying this general assumption, it has been stated that some of the proteid derivatives, as the peptones* are incompletely precipitated, and on the other hand that the flesh bases, kreatin, kreatinin, &c., are fully precipitated. The reagent in question has been recommended as the means of separating and determining them (Kœnig and Boemer, *Zeits. für Anal. Chemie*, xxxiv., 560, adopted in Prof. H. W. Wiley's "Principles and Practice of Agricultural Analysis," iii., 454).

*Dr. W. H. Halliburton, in the article 'Proteids' in Watts's 'Dictionary of Chemistry," revised edition, vol. iv., p. 331. In Gamgee's "Text-book of Physiological Chemistry," vol. ii., p. 139, it is stated that peptones are precipitated by phospho-tungstic and phospho-molybdic acids, and that these two reagents furnish the means of separating them. A similar unqualified statement is to be found in the Appendix (by A. Sheridan Lea) to Michael Foster's "Text-book of Physiology," p. 45.

Account does not seem to have been taken hitherto of the fact that some of the precipitates formed by substances of amidic character with phospho-tungstic acid are to a small extent soluble in water, and that their solubility is much increased by rise of temperature.

Classification of Substances Examined.

It has been found that the various substances on which these experiments have been made fall into three classes as follows:—

(*a*). Those which, even in pretty strong solution, give no precipitate with phospho-tungstic acid.

(*b*). Those which are precipitated at any rate in strong solutions, the precipitate re-dissolving with more or less ease on heat being applied to the liquid or on treating the precipitate with hot water, and re-appearing on cooling.

(*c*). Those which are precipitated, the precipitate not being sensibly soluble and the supernatant liquid remaining clear on being heated along with the precipitate and subsequently cooled.

Under the first head fall glycocin. alanin, leucin, aspartic acid, asparagin, glutamic acid, tyrosin, and allantoin. In the case of alanin there was a very slight turbidity not increased by using a saturated solution, suggesting the probability of a trace of some impurity being present.

Under the second head were observed glutamin, a slight precipitate, the solution easily cleared by heating, the turbidity re-appearing on cooling; betaine in strong solution, a copious white precipitate, dissolving gradually on addition of more water and heating, the precipitate re-appearing on cooling; kreatin, strong precipitate, solution cleared by heating, becoming turbid again on cooling; kreatinin, large precipitate, disappearing on free addition of water and heating, reappearing on cooling; hypoxanthine, strong precipitate, cleared up on heating, re-appearing on cooling; and carnine, well-marked precipitate, cleared by moderate addition of water and heating, reappearing on cooling. Urea also, which is not likely to occur among food materials, but possibly needs to be considered in connection with undigested residue, gave a copious white precipitate of crystalline character, cleared by heating, and the precipitate forming anew on cooling. A peptone solution gave an abundant precipitate, becoming clotted by heating, and dissolving to a considerable extent, re-precipitating on cooling.

Under the third head were found egg albumen, fibrin, casein, legumin, globulin, vitellin, myosin, syntonin, hæmoglobin, albumose, gelatin, and chondrin. In nearly all these cases the precipitate formed was bulky, taking into account the strength of the solution used, and became clotted on heating, shrinking very considerably. In the case of myosin only (in 10 per cent sodium chloride solution) was there a very slight appearance of turbidity on cooling the solution which had been heated with the precipitate.

Use of Hot Water.

As it was evidently important to ascertain with some degree of definiteness how far the precipitates formed by amidic substances of the second of these classes would dissolve in hot water, quantitative experiments were made with those which seemed to be least soluble. In each case the precipitate formed by phospho-tungstic acid in the cold was filtered off, washed with cold water, and dried at ordinary temperature (15° to 20°) over sulphuric acid. Stutzer advises that the phospho-tungstic acid precipitates be washed with dilute sulphuric acid, and Wiley recommends for the same purpose a solution of the precipitates. Of the precipitate formed by betaine, 1 part dissolved in 71 parts of water at 98·2°; of that produced by kreatin,* 1 part dissolved in 107 of water at

* The phospho-tungstic acid precipitate, formed by kreatin, white at first, darkened notably on exposure to light, looking after a while like silver chloride which had been in like manner exposed. The experiment on solubility was made with a sample which had been screened from light and was unaltered.

98·1°; of that produced by kreatinin, 1 part dissolved in 222 of water at 97·9°; of that produced by hypoxanthin, 1 part dissolved in 98 of water at 97·6°; and of that produced by carnin, 1 part required for solution 132 of water at 98·4°.

By the use of phospho-tungstic acid as a precipitant, therefore, followed by washing of the precipitate with hot water, it seems possible to effect a separation of all the simpler amidic substances from all the proteids and proteid-like bodies, except only the peptones. As regards this last group it is stated unreservedly by A. S. Lea ('The Chemical Basis of the Animal Body,' an Appendix to M. Foster's "Text-book of Physiology," 1893, p. 45), A. Gamgee ("A Text-book of the Physiological Chemistry of the Animal Body," 1893, ii., 139), and W. D. Halliburton (Watts's "Dictionary of Chemistry," revised edition, 1894, iv., 331), that the peptones are precipitated by tannic acid. The last-named writer says "completely precipitated." In one or two of the writer's own experiments, using tannic acid, an abundant precipitate was formed. This became clotted on heating, and the clear supernatant liquid showed some little return of turbidity on cooling. The writer is inclined, however, to attribute this apparent partial re-solution of the precipitate merely to the presence of a little of a proteose formed in the earlier stages of digestion and not afterwards completely removed. Assuming this view to be correct, tannic acid furnishes the reagent needed to dispose of the one case unprovided for by phospho-tungstic acid.

Details of the Method with Phospho-tungstic Acid.

The method proposed is as given in the following paragraphs. It is stated, for the sake of simplicity, first, as applicable to meat, raw or cooked. The variations required in the examination of other classes of food materials are reserved for notice afterwards.

A carefully selected and accurately weighed sample is to be ground in a glazed porcelain mortar with as much sharp-edged siliceous sand, previously heated to redness with free exposure to air, or with as much hard glass in small sharp splinters similarly ignited, as shall suffice to thoroughly subdivide the tissue and reduce it to the condition of a smooth pulp. Of this pulp, very carefully mixed, so as to insure uniformity, two aliquot parts are to be taken. In one the total nitrogen is to be determined by the well-known Kjeldahl process with the addition of potassium sulphate, as recommended by Gunning, using a rather large proportion of sulphuric acid, so that no previous drying of the sample is needed. The other part is to be digested with cold water, filtered on a nitrogen-free filter,* and the residue washed on the filter with water at the same low temperature as long as it gives up soluble matter in sensible amount. Cold water is used to avoid action on and extraction of the gelatinoids. Creatinin is quite easily dissolved, as is also sarcosine; creatin with a very fair degree of ease. Xanthin, hypoxanthin, and carnin are less soluble.†

The filtrate is then to be slightly acidified with acetic acid, heated to about 90° C., and again filtered from any coagulum produced. A little more sand or pulverised glass may with advantage be stirred in before bringing it on to the filter the second time.

To this second filtrate is to be added an acidified solution of phospho-tungstic acid as long as a precipitate continues to form, avoiding any very large excess of the reagent solution. With a moderate amount of sand or pulverised glass added, to prevent the formation of a dense clot, the liquid and precipitate are to be heated to about 90° C., filtered, and the precipitate washed thoroughly on the filter with water at about the same temperature. This third filtration may be carried out on the same filter already used for the second, but as a general rule it will be found better to use a new filter, thus avoiding possible delay due to partial drying of the previously used one and subsequent clogging of its pores.

Assuming now that nitrogen is present in the sample under examination only in the two forms of proteids and simpler amidic compounds, the three (or two) filters used and their contents are to be submitted to the Gunning-Kjeldahl process for the determination of proteid nitrogen. By subtraction of this from the total nitrogen previously determined the amount of this element present in the simpler amidic compounds will be obtained.

In cases involving the presence of ammonia or its salts, nitrates, or alkaloids, the nitrogen occurring in these forms must, of course, also be deducted from the total nitrogen before recording the residue as nitrogen of the simpler amides and amido-acids. In like manner a separation of lecithin, when present, may be effected by the use of ether as a solvent,* a determination of phosphorus made the basis of a calculation of lecithin nitrogen, and this in turn extracted from the total nitrogen found.

When peptones are present, these are to be precipitated by tannic acid from the solution which has been acidified with acetic acid and heated. After this has completely cooled down, and before adding phospho-tungstic acid, the filter on which the tannic acid precipitate is collected and washed with cold water is, with its contents, to be submitted to the modified Kjeldahl process, and the nitrogen obtained counted as part of the proteid nitrogen.

The several filters and precipitates from which the proteid nitrogen is obtained may either be treated separately by the Kjeldahl process or, preferably, may all be brought together and submitted to this process in a single operation. If the latter course be pursued, it will be well to introduce each filter with its contents as soon as washed into the strong sulphuric acid, so as to avoid any possible decomposition and loss of nitrogen as ammonia until all the filters have been brought together and the moist combustion process can be proceeded with.

When proteoses are present it may be well to make a check determination of their amount by saturation of the aqueous solution, after acidification with acetic acid, heating, and subsequent cooling, with zinc sulphate (as suggested by Boemer, *Zeit. Anal. Chemie*, 1895, xxxiv., 562), and determining nitrogen in the precipitate so formed by means of the Kjeldahl process.

When gelatinoids are present, as may be the case with soups, stews, and meat extracts, hot water may be used at once for solution or washing the original material, and this with the advantage of facilitating the extraction of the less soluble simpler amides and amido-acids. These are, as a rule, more easily dissolved in the presence of a little free acid; hence acidification at an early stage of the treatment is advantageous. In a case in which tyrosin might be present, as in some vegetable materials, and possibly among unabsorbed residua of food, the use of hot water and the presence of free acid would greatly increase the solubility of this substance.

In food of vegetable origin where much starch is present it will be better to avoid the use of hot water at first, so that the solution may not be loaded with viscid material, rendering filtration difficult.

In all cases in which the food material to be examined is already fluid from the presence of water—as, for instance, soup, milk, and the like—filtration will, of course, at once be resorted to, being almost always much facilitated by the addition of sand or pulverised glass, and only such further quantity of water will be used as is required for washing the undissolved matter left upon the filter.

In the presence of fat in large quantity, it may be well first to remove this, or most of it, by extraction with ether. The simpler amidic substances are, as a rule, insoluble in ether, but by way of precaution the ethereal solution of

* The ease with which filtration may be effected is much increased by the presence of the sand or crushed glass.

† Hypoxanthine, 1 part in 300 of water. The solubility of carnine does not seem to have been recorded till now. The writer has found it to be 1 part in 312 of water at 15·3° C.

* Extraction with the ether alone will remove only a portion of the lecithins. A mixture of ether and alcohol should follow the ether in order to secure a complete extraction.

fats might be shaken up two or three times with acidified water, and the watery fluid evaporated and tested for nitrogen.

In regard to the method of reporting results, the most important point is the separate statement of the amount of nitrogen present in the form of proteids and their more closely related congeners and in the form of the simpler amides and amido-acids. But in attempting to calculate from the nitrogen found under these heads the actual amount of the proximate nitrogenous constituents of the food material examined, the question arises—What factor should be used by which to multiply the nitrogen found in each case?

Factors for Calculation of Total Nitrogen.

The error noticed by Professor Wiley ("Principles and Practice of Agricultural Analysis," 1897, iii., 551) as involved in the multiplication of the total nitrogen of a sample of meat by 6·25, and the assumption that the product represents the true quantity of nitrogenous matter, is not restricted to the use of the same factor for the proteids and flesh bases. While the multiplier should be a much smaller one for the latter, it also confounds under a single head these two classes of material, unquestionably possessing very different nutritive values.

It is evident that for each substance examined, or at any rate for each class of generally similar food materials, there should be made a qualitative investigation of the simpler amidic constituents present, and if possible a roughly approximate estimate of the proportions in which they severally occur; also it is clear that the factor to be used in calculating the nitrogenous constituents to be reported under each analysis should be decided by such preliminary investigation. In the light of present knowledge the writer is inclined to suggest the following numbers:—

For proteids and allied substances, multiply nitrogen found by 6·25, as usual at present.

For flesh bases and simpler amides of animal origin in food materials, multiply by 3·05.

For simpler amides and amido-acids of vegetable origin in food materials, multiply by 5·15.

For mixed amidic constituents of unabsorbed solid residua in digestion experiments, multiply by 9·45.

As a matter of general practice, in all statements of the results of nutrition experiments the rule should be invariably observed to give the actual amounts of nitrogen obtained by analysis, whatever calculated conclusions be afterwards deduced therefrom; so that, with further knowledge of the nature of the proximate nitrogenous constituents present, the factor used in calculation may be changed, if such change seems to be called for, while the original experimental work still retains its value.

In concluding this report, the writer wishes to express the hope that the method suggested, which seems to carry with it some improvement upon present practice and in a fairly simple and easily applied form, may be tried with yet other amides and proteids than those experimented on by him, and that any special difficulties which may be encountered with particular articles of food may be investigated. Especially is it desirable that the variations be studied which may prove to be necessary in dealing with vegetable instead of animal materials. The latter have been chiefly kept in view, in accordance with the instructions of the letter of authorisation under which this investigation has been conducted.

On the Isomeric Benzoylketoximes.—J. Schmidt.—The author has prepared a liquid isomer of benzoylketoxime, by reacting with chloride of benzoyl on the soda derivative of acetoxime. The reaction should be carried out in the cold; sodium is added to acetoxime and ether; when all the sodium has changed into a white crystalline mass, it is filtered and washed with ether; pure chloride of benzoyl and anhydrous ether are then added in the cold. When the reaction is finished, filter and evaporate *in vacuo*. The solid isomer is gradually deposited, and can be easily removed.—*Berichte.*

THE SOUTHAMPTON BACTERIAL SYSTEM AT SOUTHWOLD.

Mr. Fredk. Ball, Civil Engineer, Borough Surveyor of Southwold, reports that, in consequence of the Sewage Works at the time of his succession to the office of Borough Surveyor of Southwold being inadequate, Mr. Candy, of the International Purification Syndicate, was instructed to submit a scheme for the Bacterial treatment of the sewage upon the Polarite Oxidising system, in order to test—which it was decided to utilise—one of the three existing precipitation tanks. The Southwold sewage, it should be mentioned, is excessively foul and concentrated, owing to the small consumption of water.

The tank was divided into two compartments, to form an anaërobic sludge digesting bed and an aërobic or polarite oxidising bed.

Crude sewage is admitted to the detritus chamber wherein the grit is deposited, and paper and floating solids are arrested until sufficiently disintegrated to be carried into the anaërobic bed through slotted wooden troughs laid below the surface of the anaërobic bed, being thus evenly distributed.

This bed consists of large cobble stones from the beach laid to a depth of about 4 feet. On the top of the cobbles the slotted wooden troughs are laid, and the whole covered over with gravel so that anaërobic conditions are obtained.

The liquid sewage passes equally downwards through the bed, and is collected into a brick channel with iron outlet pipes, fixed in the top and rising above the level of the inlet troughs, but not up to the level of the top fine gravel, which thus presents a clean and pleasing surface, expensive arching over being altogether avoided.

These pipes discharge into an open trough which feeds the self-propelled revolving sprinklers and aërators (Candy's patent) that deliver the anaërobic effluent on to the rapid oxidising polarite bed, which effects the final purification by oxidising the soluble impurities and nitrifying the ammonia.

This system of working Bacteria beds constitutes a marked advance in efficiency and economy over the contact method of filling, stagnating, drawing off, and resting.

The quantity of sewage treated is 500 to 600 gallons per square yard of filtering area per twenty-four hours; the aërobic beds are only 2 feet thick, on account of want of fall.

The sewage of Southwold, as before stated, is very strong, as indicated by analysis, but the effluent is also shown by analysis to be an excellent one.

The result of a series of analyses of Southwold polarite oxidising Bacteria effluents shows from 92 to 98 per cent of purification, with average nitrates 3·36 grms. per gallon.

Mr. Ball reports that, in his opinion, the shallowness of the bed combined with the high speed of filtration and the foulness of the sewage render the results obtained satisfactory in the highest degree, and constitute a great achievement in economical sewage purification.

The system has been in operation since the 16th of April last, and there are no signs of sludge or choking of the bacteria beds. The chief object in adopting this bacterial system was to obtain the abolition of sludge. So successful has it been that arrangements are being made to treat the whole of the sewage by this system.

Apart from the chemical evidence of the purity of the effluent, one has but to view the old and the new systems, working side by side, to realise the advantages of the latter.

In the old system there are large tanks full of sewage covered with foul-smelling septic scum, and tons of sludge to be disposed of. In the new system no sewage is

visible but the comparatively clear liquid periodically discharged through the revolving sprinklers.

In the place of the sewage scum there is the clean surface of the polarite oxidising bed, and there is also the untold advantage of the absence of sludge.

CORRESPONDENCE.

SUPERCOOLING OF PHOSPHORUS.

To the Editor of the Chemical News.

SIR,—The supercooling of water is a well-known phenomenon, but it is somewhat difficult to show as a lecture experiment, as it requires a good deal of preparation. The supercooling of liquid phosphorus, on the other hand, is exceedingly simple to demonstrate. If a piece of phosphorus be melted under a strong solution of caustic soda or potash, as in the preparation of phosphoretted hydrogen, it will remain liquid apparently for an indefinite time; at any rate, I have kept some four days in that condition. Its temperature can be taken roughly by immersing a thermometer bulb in it, and it will bear moderate shaking or motion without becoming solid. If violently shaken it solidifies suddenly; also if an attempt is made to pour it out of the vessel. Of course, the body of solution in which it is placed prevents any noticeable rise of temperature on solidification when dealing with only a small quantity of phosphorus.

I should imagine that chemical action has largely to do with the retention of the liquid condition, bubbles of PH_3 being given off continually, even at temperatures of 8° or 9° C. Still, whatever be the causes, the fact remains that one can obtain and keep phosphorus in a liquid state at such a temperature.—I am, &c.,

E. G. BRYANT, B.Sc.

13, Jubilee Place, Pontefract,
October 8, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 13, September 25, 1899.

Trimethylene.— M. Berthelot. — Trimethylene and propylene are an example of two gaseous isomers at ordinary temperatures. These substances are similar with regard to their condensation and chemical reactions, but the heat of formation and heat given out during combination differ considerably. The author has studied—(1) The reaction of bromine on the two isomers; (2) the action of zinc chloride on normal propyl alcohol and on trimethylene; (3) the action of sulphuric acid on the propylic alcohols; (4) the comparative reactions of zinc on the two isomeric bromides; and (5) the action of a temperature approaching 500° on propylene and trimethylene. He finds generally that trimethylene is less stable than propylene, and is transformed into its isomer, not only by heat, but even (more or less partially) by the influence of reagents employed for the formation of the bromide. These results, for which the thermo-chemical numbers are given, were predicted.

Journal de Pharmacie et de Chimie,
Series 6, Vol. ix., Nos. 10 and 11.

These numbers contain no matter of chemical interest.

No. 12.

Rectification and Preservation of Chloroform.—V. Masson.—The rectification of chloroform comprises the following operations:—(1) Washing with distilled water; (2) treatment with 2·5 per cent sulphuric acid for two or three days; (3) treatment with 3 per cent soda-lye for three or four days; (4) washing with distilled water; (5) treatment with pure melted coarsely-powdered chloride of calcium; this should be agitated for three or four hours, and poppy-seed oil then added; (6) distillation. Poppy-seed oil possesses to a very high degree the property of preventing the decomposition of chloroform—one-thousandth part of the oil being sufficient to prevent any alteration of the chloroform when exposed to direct solar radiation, while the addition of two-thousandths of poppy-seed oil has kept chloroform intact for three years.

Combination of Phenylhydrazine with Bisulphite of Sodium.—M. Pastureau.—The author has noticed that a solution of bisulphite of sodium gave, when treated with phenylhydrazine, a crystalline precipitate very soluble in water. This precipitate was washed several times with ether, then dried on a porous porcelain plate; it occurs in the form of colourless flakes. By a second crystallisation in water, slowly and carefully evaporated at 50—60° the substance was obtained in the form of colourless needles radiating from a centre. Analysis gives the formula $SO_3Na,2(N_2H_3.C_6H_5)$; it is therefore a double sulphite of sodium and phenylhydrazine.

MISCELLANEOUS

Pelletier-Caventou Monument.—We are surprised to hear from the treasurer of this committee (M. Bocquillon-Limousin, 2 *bis* rue Blanche, Paris) that until the other day no subscription to the monument had been received from England or any other part of the British Empire. The discoverers of quinine deserve to be honoured by all English-speaking people, for, as M. Bocquillon-Limousin says, "England, by reason of her numerous colonies, should be one of the nations which has profited the most from these benefactors to mankind." This is quite true, and the reason why English subscribers are laggard is that we have not the monument-admiration sense so highly developed as the French. It is not too late to subscribe, and we hope there will still be a response from this side of the Channel.—*Chemist and Druggist.*

On the Identity of α-Digallic Acid and Tannin.—P. Walden.—Flawitsky has already shown that tannin is dextrogyre; $\alpha_D = +60°$ in aqueous solution. The author is of opinion that tannin is not a definite compound, but a mixture containing a compound in variable proportions, with a higher rotatory power, $\alpha_D = +75°$; α-digallic acid is, on the contrary, inactive; further, it softens at 120° and decomposes at 150°, while tannin melts at 110°—115°. After considering various properties, the author concludes that tannin and α-digallic acid are altogether different bodies.—*Berichte.*

Influence of the Formation of Salts on the Saponification of the Amides and Ethers by means of Alkalis.—E. Fischer.—The research made by the author on the purine group have led him to the conclusion that the saponification of the amidised or ether salt groups is the more rapid as the compound formed is more neutral; or, in other words, that the formation of a salt retards the saponification. Trimethyluric acid 1.3.9 is attacked much more rapidly than the dimethyluric acids. Cyanuric acid is only partially decomposed when heated in a sealed tube for eight hours to 100°, with normal potash, but isocyanurate of methyl is attacked very rapidly under the same conditions, being transformed into trimethylbiuret, $C_6H_9N_3O_3 + H_2O = C_5H_{11}N_3O_2 + CO_2$. This latter body crystallises in benzene in acicular prisms, fusible at 126°, soluble in water and alcohol, but very slightly soluble in ether and ligroin.—*Berichte.*

Estimation of Sulphur in Roumanian Petroleum.—G. Filiti.—Among the most important methods for the estimation of sulphur in organic substances may be mentioned that of Carius, the method of decomposing the substances and their oxidation by chlorate of potash and carbonate of soda, the method of oxidation with binoxide of sodium, &c. All these methods have certain advantages in special cases, but become almost useless when we have to deal with the estimation of sulphur in volatile organic substances, and in which the quantity of sulphur is extremely small. Before succeeding in effecting the estimation of sulphur by his new method, the author had tried all the others without success; he then took up the line indicated by Langbein, who showed, by the combustion of saccharine in a calorimeter, that the sulphur was completely oxidised in the presence of oxygen and of a small quantity of water. He applied this method to the estimation of sulphur in petroleum and other bodies. By this method, long and difficult operations and all causes of error are avoided. The advantages of this method are—(1) The possibility of operating on a quantity of material twenty times greater than can be used by the Carius method; (2) the products obtained only contain traces of nitric acid, the precipitation of the sulphur by chloride of barium is effected in a direct and immediate manner. It must be well understood that in using this method it is absolutely necessary to be certain of the purity of the reagents and of the cleanliness of the apparatus.—*Bulletin de la Soc. Chim. de Paris*, Series 3, vol. xxi., No. 7.

NOTES AND QUERIES.

**** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Public Analyst.—Can any reader inform me what the necessary qualifications are for recognition as an Analyst under the Food and Drugs or other Public Health Acts?—B.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Microscopical, 8, "British Trap-door Spiders.' Lantern Demonstration by F. Enock F.L.S., F.R.S.

SECOND EDITION, 8vo, 9s.

OUTLINES OF THEORETICAL CHEMISTRY.

By LOTHAR MEYER,

Professor of Chemistry in the University of Tübingen.

Translated by P. PHILLIPS BEDSON, M.A. (Dun.), D.Sc. (Lond. et Dun.), B.Sc. (Vic.), F.I.C., F.C.S., Professor of Chemistry in the Durham College of Science, Newcastle-upon-Tyne; and W. CARLETON WILLIAMS, B.Sc., F.I.C., F.C.S., Professor of Chemistry in the University College, Sheffield.

With a Preface by the Author.

*** In preparing a second edition of the translation of Meyer's "Outlines of Theoretical Chemistry," the translators have availed themselves of the second edition of the German, published in 1893, a few years before the death of Lothar Meyer. Whilst the original form has been still retained, they have, by occasional footnotes and appendices, sought to bring the book up to date.*

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SOME EXPERIMENTS TO OBTAIN, IF POSSIBLE, DEFINITE ALLOYS OF PLATINUM AND PALLADIUM WITH CADMIUM, ZINC, AND MAGNESIUM.*

By Professor HODGKINSON, Captain WARING, R.A., and Captain DESBOROUGH, R.A.

THAT platinum alloys with zinc has been noticed by several observers ("Gmelin-Kraut," [3], 1193, refers to Gehlen, Fox, Murray, and others; Deville and Debray, *Ann. Chim. Phys.*, [3], lvi., 430; Boussingault, *Ann. Chim. Phys.*, [3], liii., 420).

Generally it is stated that the metals unite with energy, and that when the combination is heated until infusible the compound is representable by the formula Pt_2Zn_3. Deville and Debray, after heating the zinc alloy with dilute sulphuric acid, obtained a black powder containing 31 per cent zinc and a little free platinum.

Our method has been to submit a weighed amount of platinum to the vapour of the volatile metal, maintaining the platinum and compound formed all the time at a temperature above the boiling-point of the particular volatile metal.

Two plans have been tried: one carrying the vapour with hydrogen, another heating the metals in a vacuum. In both cases a very infusible Jena glass tube was employed.

In each form of experiment a weighed quantity of platinum (or palladium), in thin foil, was contained in a porcelain boat. Almost touching this was another boat containing the volatile metal in very considerable excess. The region about the two boats was heated very strongly in a powerful combustion furnace, and in the case where hydrogen was used the current of gas passed over the zinc, or other metal, towards the platinum.

When the heating was conducted in a vacuum, the Sprengel pump was attached at the platinum end of the tube, so that the vapour could be drawn over the platinum. The heating was in each case continued for some hours (three to four). After cooling, the boat with platinum alloy was weighed.

Cadmium.— Vapour carried by Dry Hydrogen.—The alloy or compound formed corresponds almost exactly to the formula $PtCd_2$. This is given by the amount of cadmium taken up by the platinum. (In one experiment, 0·5832 of platinum absorbed 0·6892 cadmium).

The relative weight of the compound at 15° was found to be 13·53, and the calculated for an alloy of the composition $PtCd_2$ is 13·59.

The alloy is white, crystalline, and very brittle. When heated to full redness in a vacuum tube, scarcely any cadmium was sublimed; the loss in weight was inappreciable.

In nitric acid some platinum was dissolved along with the cadmium. Heated in a vacuum tube, the same compound is formed.

Platinum and Zinc in Hydrogen.— The action was slower than with Cd. In one experiment 45·57 per cent of zinc was absorbed. This was a particularly long exposure—nearly five hours—and the temperature was not much above the melting-point of the zinc. An alloy $PtZn_2$ requires 40 per cent Zn. On heating this 45 per cent alloy for two hours in a vacuum tube some zinc was distilled off, leaving a residue containing 44 per cent Zn. It was now heated until the Jena glass tube began to give way. The Sprengel was keeping up the vacuum during the heating. More zinc distilled off, and after two hours of strong heating the residue was found to contain 24·45 per cent zinc; this is nearly PtZn, which requires 25 per cent Zn. It seemed hopeless to try further in glass tubes. This alloy is crystalline and extremely brittle, and dissolves in acids similarly to the cadmium alloy. Heated side by side in a vacuum tube the same alloy of platinum and zinc seemed to be formed. The process was very slow, possibly because the zinc vapour travels but a little way alone.

Platinum and Magnesium.—This was the most difficult, as, at the temperature employed, the magnesium vapour is almost entirely absorbed by the glass of the tube and by the porcelain boat. Some magnesium was distilled in a vacuum; this was placed in a porcelain boat lined with MgO, the platinum was placed as close as possible, and the whole was heated until the Mg was melted; a gentle current of very dry hydrogen was then kept up for some hours. An extremely friable crystalline alloy was produced. From the amount absorbed it corresponds very nearly to the formula $PtMg_2$. These experiments are being repeated.

Palladium.—The experiments with this metal and cadmium and zinc have so far failed to give any result. Very little cadmium seems to be taken up by palladium, either when heated in a vacuum or in a current of hydrogen; what little is taken up distils away very easily. It is possible to keep a piece of palladium foil for two hours in cadmium vapour without change. There is a little more tendency for zinc to alloy.

Nickel behaves very much like palladium in this respect. Some electro-deposited Ni foil was heated for several hours in cadmium vapour without appreciable change in weight.

Ordnance College, Woolwich.

* Read before the British Association (Section B), Dover Meeting, 1899.

IODINE IN SEA WATERS AND FRESH WATERS.

By A. GAUTIER.

THE examination of the air and its dust has enabled me to establish the fact, which has been alternately affirmed and then denied, that iodine is really found in the air, but that it is completely fixed in the organic state in the matter caught by plugs of glass-wool. Sea air contains about thirteen times as much iodine as that found inland; aërial iodine appears thus to come principally from the sea, which is continually giving up, in the form of aqueous dust, a portion of its iodised elements.

I have proved the complete absence of alkaline or alkaline-earthy iodides in the air, even in several hundred litres collected on the surface of the ocean, and this result was not found without surprise, for sea air contains not only the microscopic organisms which abound on and near the surface of the sea, but also the dissolved salts which the winds are continually carrying off in the form of fine spray. It therefore seemed to me that a part of the iodides from the sea water thus carried by the winds should be found either on the glass-wool plugs when the air was filtered, or in the concentrated solution of potash through which it afterwards passed.

What can be the quantity of alkaline or alkaline-earthy iodides thus carried by the winds? It is proportional to their concentration in the superficial sea water. When I attempted to calculate this concentration, according to the already published analyses of sea water, I was immediately stopped by divergences almost as great as those which I met with for iodine in the air. From the time that J. Boussingault declared that it was almost impossible to detect iodine in sea water, and

Stephenson Macadam asserted that several gallons were required to find 1/500,000th of a grain, down to Koettstorffer, the last chemist who dealt with this question, and who found 1 m.grm. in 50 litres, the matter has remained entirely unsolved. In fact, not only the presence of iodine in appreciable quantities in sea water still remains uncertain, but even the existence of this iodine in the form of mineral iodides does not rest on any direct proof, although it has been generally admitted by analogy with what occurs with chloride of sodium. The object of the present paper is to show that the water of the open sea, or at least that at or near the surface, *does not contain a trace of alkaline or earthy iodides;* that iodine is always found in easily weighed quantities, but *that it exists entirely in the organic and organised state*—a circumstance which has been overlooked up till now, and to which is due the contradictory opinions expressed on the quantity, and even on the appreciable presence of iodine in sea water.

During fine weather in November, 1898, in the English Channel at 40 kilometres from the coast, I took 12 litres of water with the usual precaution, and treated it in my laboratory in the following manner:—Pure carbonate of potash was added in the cold as long as a cloudiness appeared, then 0·3 grm. to 0·4 grm. of caustic potash; this was then evaporated without filtering, until its salts commenced to crystallise; it was then mixed, before completely cooling, with alcohol, at 83°: this precipitated the greater part of the salts. The alcoholic solution containing the whole of the alkaline or earthy iodides is evaporated, when it is reduced to about one-twelfth of its volume; it is allowed to cool, the solution is neutralised with dilute sulphuric acid: it is then again made alkaline with a few drops of pure potash, and precipitated a second time with alcohol at 90°. The filtered solution is evaporated to dryness, ignited to destroy the organic matter, and the residue taken up with water and filtered. The aqueous solution thus contains, in a very small volume, the whole of the iodine and bromine from the iodides and bromides in the sea water.

To separate the iodine we have recourse to J. Krutwig's method, perfected by Dechan; it consists in distilling the iodobromised solution with a very concentrated solution of bichromate of potash. The iodine *only* passes over completely and from the beginning with the steam, which may be condensed in 1 or 2 c.c. of pure dilute potash. When 10 to 15 c.c. have been distilled, the potassic liquor is supersaturated with dilute sulphuric acid, and the iodine is estimated as has been described for its determination in air.

Now, when we thus attempt to estimate the iodine in 5 litres of sea water, *we do not find a trace.* Further, I feel certain that by following this method we could recover integrally 0·0005 grm., or even 0·0002 grm. of iodine, added in the state of iodide or iodate* in 1 litre of salt water having the average composition of sea water.

Convinced by these experiments of the absence of mineral iodides in sea water, and remembering what I had already noticed with air, it occurred to me that the iodine might exist in the form of organised corpuscles (microscopic algæ, zoogloæ, &c.), or as organic compounds (such as iodised nuclea, spongine, iodothyrine, &c.), iodised principles in which all the characteristics of mineral iodine have become latent.

To decide this question I took up the residue of 5 litres of sea water which remained insoluble in dilute alcohol, and in which I had vainly sought for mineral iodine, and, after having moistened it with concentrated potash, and even adding pure solid potash, I fused the whole in a pure nickel crucible to destroy all the organic matter. Under these conditions an alkaline odour was given off, indicating the destruction of complex nitrated substances. On cooling, the crucible was placed in ice and water added; it was then carefully neutralised with dilute H_2SO_4, and precipitated with alcohol at 90°. The alcoholic solution is filtered, the alcohol driven off, and the iodine tested for in the residue. I thus found—

Total organic iodine in 5 litres ..	12·00 m.grms.
That is—	
Total organic iodine per litre	2·40 ,,

Thus iodine does exist in sea water in an easily weighable quantity, but the iodised matter in this water is quite insoluble in alcohol in the presence of caustic alkalies, and the iodine does not appear until after fusion with potash: this element is thus found in the water, in the latent form, and cannot be detected until all the organic matter is destroyed—then only can it be weighed, and 20 grms. of sea water is sufficient.

But we must go further, and enquire if the iodine is contained in sea water entirely in the form of microscopic algæ, sponges, &c., or whether a part of this element enters into the constitution of an organic substance soluble in water.

To decide this point I carefully filtered 5 litres of very transparent water from the open sea, on a small filter of Sèvres biscuit porcelain. I soon noticed that a semi-organised glutinous material was deposited on the surface of the porcelain comparable to that secreted by many microscopic algæ. This matter was examined by M. Bornet; he found that it was formed of a slimy substance, in which was entangled various organic and mineral *débris;* he also recognised a quantity of vegetable matter, flagellæ, rotifera, but, above all, microscopic algæ of the family of diatoms. This organic deposit did not appear to amount to 0·01 grm. in the wet state.

Iodine was tested for in the portion obtained from 5 litres of sea water. There was found—

Iodine from organic matter in 5 litres	2·60 m.grms.
That is—	
Organised iodine in 1 litre of water ..	0.52 m.grm.

In its turn the sea water which had passed through the porcelain filter was made alkaline, evaporated, and the iodine estimated. After fusion with potash, as described above, there was found—

Organic iodine dissolved in 1 litre of sea water..	1·80 m.grms.

The result of these estimations shows that 1 litre of water from the open sea contains in the organic and organised forms:—

Insoluble organised iodine	0·52 m.grm.
Dissolved organic iodine	1·30 ,,
Total iodine per litre	2·32 m.grms.

It has already been seen that we found 2·40 m.grms. of total iodine per litre of sea water, a figure which confirms these latter results. We may thus conclude:—1. That water from the open sea, taken at or near the surface, does not contain a trace of mineral iodides. 2. That in this water the whole of the iodine exists in the form of organic compounds. 3. That a part of this organic iodine, about one-fifth, is fixed in the microscopic organisms which live on or near the surface of the water. 4. That four-fifths of the iodine is found in the state of soluble organic compounds.

The iodised organic matter of sea water merits serious study; this I have only just commenced. I have already found that it can be partially separated by dialysis from the salts which accompany it. The part remaining on the dialyser contains a complex organic substance, at once carbonated, nitrated, and iodised, and rich in phosphorus and manganese. Is this substance derived from the algæ which, so to speak, give it off? Or is it, on the contrary, the primitive organic matter from which they

* The iodine of the iodates can be dissolved in dilute alcohol if the solution is made alkaline by potash.

take their birth? This question has not yet been answered.

Partly dissolved in water, and partly fixed by microscopic organisms, these complex iodised and nitrated compounds from the sea accumulate near the shore, and and are deposited as foam. After bathing they adhere to the skin by which they are absorbed later on, benefitting us by their specific action. From observations which I have made in the course of this investigation, I find that analogous phenomena occur with bromine; a notable portion of this element is also found in sea water in the organic state.

There remains to be explained whence the organic iodine in sea water comes, as well as that which is fixed in the organisms and that in solution; evidently it can only come from below, either in the form of iodised springs, volcanic emanations, or by solution of submarine rocks. Numerous terrestrial iodised springs are known (Saxony, Toeplitz, Heilbrunn, &c.), and there is no reason to doubt that similar springs exist in the sea. On the other hand, submarine volcanic eruptions have been observed in every ocean: now it has long been established that volcanic products, such as lava, contain iodine; finally iodine exists in granitic and even calcareous rocks, and these become dissolved in the salt water by the action of carbonic acid and corrosion. This mineral iodine dissolved in the deepest parts of the sea disappears in the upper layers, where the action of light permits organisation and life.

But these marine beings, and particularly salt-water algæ, are not the only iodised organisms. I have found that iodine always exists in appreciable quantities in terrestrial and fresh-water algæ. These algæ can only take their iodine from the waters in which they live. This makes us ask in what form this iodine is found, if it also exists in fresh water in the organic state, and, if so, if it has been missed, as in sea water, by the chemists who have attempted to find and estimate it. I will only take two river waters in which the estimation of iodine has already been attempted—that of the Seine and that of the Marne (*Comptes Rendus*, 1850—1855). After having filtered them through porcelain, to separate the organisms, I estimated the iodine in the part collected on the filter, and also in the filtered water after destroying the organic matter in the residue by fusing with potash. The results per litre of water were as follows:—

	Iodine in organisms.	Soluble iodine.	Total iodine.
	M.grm.	M.grm.	M.grm.
Seine water	0·0025	0·0025	0·005
Marne water ..	0·002	0·0011	0·0031

These waters thus contain a small quantity of iodine, partly soluble: towards 1852 M. Chalin announced the presence of iodine in river waters before I did; we obtained almost identical results. As he worked on simply filtered water, and did not take up his residues with melting potash to destroy the organic matter, it follows that the iodine in these river waters is for the most part soluble in the form of alkaline or earthy iodides.

Whence comes the iodine in fresh water? It comes partially from the air, as we have seen that sea air loses 12/13ths of its iodine when over the land. But it comes principally from the earths and rocks over which the water flows. Iodides have been observed in certain calcareous rocks (the jurassic earths near Lyon, dolomite in Saxony and Savoy, the miocene rocks near Montpellier). But it exists especially in the primitive rocks, where the micas and the micaceous rocks contain numerous chlorised, fluorised, and iodised apatites; we know, in fact, that iodine has been extracted commercially from phosphorites, whose origin is these apatites, as well as from the warm sulphurous waters which emerge from these rocks.

The importance of the estimation of small quantities, both in air and water, of an element so active as iodine, admits of no doubt; this body is indispensable to organised life, but the smallest proportions suffice. We know that the total extirpation of the thyroïd gland, which in man contains no more than 30 m.grms. of iodine, is rapidly followed by death, but that it suffices to leave the patient an insignificant quantity of this gland to maintain its normal function. The influence of small quantities of iodised organic matter on our system is not more mysterious than that of the infinitesimal quantities of silver and copper which destroy life in certain moulds and algæ, or the imponderable amount of zinc necessary to the development of *Aspergillus niger*. Facts of this kind occur in the case of living beings with respect to manganese, iron, fluorine, &c. It is therefore necessary in physiological problems to use the most delicate methods of analysis. In the case of iodine it should be sought for in foods and in water, more especially in all sulphurous, chloridised, and ferruginous mineral waters, where the existence of organic iodine might falsify the results.—*Bull. Soc. Chim.*, Series iii., vol. xxi., No. 12.

LIQUID AIR AS AN ANALYTIC AGENT.*

By Professor DEWAR, M.A., LL.D., F.R.S.

The increasing importance of low-temperature research is shown by the gradual development of the applications of liquid air for scientific and other purposes. The much larger apparatus now used in the production of the liquid enables experiments to be made on a more imposing scale.

Liquid air poured from a tin can, filled by being dipped into a 5-gallon jar filled with the liquid, into a large silver basin heated to redness, remained apparently as quiescent at this high temperature as in cooler vessels, and maintained a spheroidal condition, just like other liquids. The temperature of the liquid air was about −190° C., or 83° absolute, while the vessel in which it was placed had a temperature of 800° C., or 1073° Ab. In other words, between the wall of the silver vessel and the liquid air there was a difference of temperature of 1000° C., twelve times the absolute temperature of the liquid.

Liquid air can be of great service in the qualitative separation of mixtures of gases. With the object of ascertaining the proportion *of any gas in air that is not condensable* at about −210° C. under atmospheric pressure, *or is not soluble in liquid air* under the same conditions, a series of expe.iments was made with the following apparatus:—

A cylindrical bulb of a capacity of 101 c.c., marked B in figure, had a capillary tube sealed into it terminating in a three-way stopcock, as shown at E. The parts marked C and D consist of soda-lime and sulphuric acid tubes for removing carbonic acid and water. The stand marked G holds the large vacuum test-tube into which B is inserted, and which contains liquid air maintained under continuous exhaustion. As this low temperature had to be kept steady from one to two hours, while at the same time the bulb B had to be completely covered with liquid air, it was necessary to arrange some means of keeping up the liquid air supply without disturbing the apparatus. The plan adopted is shown at H, which is a valve arrangement which can be so regulated as to suck liquid air from the large vacuum vessel A, and discharge it continuously along a pipe into the vacuum test-tube G, the latter being kept under good exhaustion. In working the apparatus, the tube I is connected to a gasometer containing 10 cubic feet of air, so that the volume of air condensed in each experiment may be observed. This was generally from 2½ to 3 cubic feet. If there is a very small proportion of some substance not liquefiable or soluble in liquid air, then we should expect the vessel B would not fill up com-

* A Lecture delivered before the Royal Institution of Great Britain, April 1, 1898.

pletely into the capillary tube. This is, however, exactly what does take place. After forty minutes' cooling, the vessel B and the cool part of the tube were filled with liquid. In this experiment some 80 litres of air were condensed, and any accumulated uncondensed matter must have been concentrated in the upper part of the capillary tube, which had a volume of 0·5 c.c. Under the conditions, therefore, the material looked for must be less than 1 part by volume in 180,000 of air.*

To test the working with an uncondensable gas added to air, a volume of 10 cubic feet was taken in the gasholder, and to that 500 c.c. of hydrogen were added. This is in the proportion of less than 1 in 500. Even after two hours' cooling, the tube B could only be filled four-fifths. In order to prove that the gas accumulated in the upper part of B was hydrogen, the three-way stopcock at E was turned, and the temperature allowed to rise, so that the gas was expelled from the evaporation of the liquid air and collected over mercury as shown at F. The gas thus collected was easily combustible and consisted chiefly of hydrogen. The amount of hydrogen was then reduced to 1 part in 1000 of air, and it was found that after one-and-a-quarter hours' cooling the bulb B had filled to within a ½ c.c. of the capillary tube. A new sample of air, containing 1 part of hydrogen in 10,000 of air, filled the bulb B completely as if it were ordinary air.

It appears from these experiments that 1 part of hydrogen in 1000 of air is just detectable in the form of an uncondensable residue. As the 80 litres of air condensed contained some 80 c.c. of hydrogen, it appears that 100 c.c. of liquid air at from $-200°$ to $-210°$ C. had dissolved nearly all this gas; in fact, that 20 c.c. of hydrogen at the low temperature is dissolved in 100 c.c. of liquid air, and can only be detected by examining the first sample of gas boiled off or extracted by lowering the pressure on the liquid. In the Paper on "The Liquefaction of Air and Research at Low Temperatures" (*Proc.*, 1895, xi., 221), it was shown that if hydrogen containing a small percentage of oxygen were employed for the purpose of getting a hydrogen jet, the liquid collected from it was oxygen, containing, however, so much hydrogen dissolved in it that the gas coming off for a time was explosive.

Coal-gas, which is a mixture of hydrogen, marsh-gas, carbonic oxide, and various illuminating gases and impurities, after passing through a coil of pipe surrounded with carbolic acid for the purpose of condensing the vapours of benzol, naphthalene, &c., when supplied to a tube similar to B, surrounded by boiling liquid air, gave a liquid and gaseous portion at the lowest temperature. It was possible to condense in this way all the constituents of coal-gas, and to separate them after liquefaction by fractional distillation, except carbonic oxide and hydrogen.

Ultimately, however, the carbonic oxide would be condensed, and hydrogen be left alone in the gaseous state. Similarly, any gas less easily condensed than air could be separated from a mixture of the same with air. Hydrogen present in air to the extent of one in a thousand is just detectable, but smaller quantities escape direct observation owing to solution in the liquid. In order to press this inquiry a little further, some natural gas known to contain a different constituent, like helium, suggested itself as being worthy of trial. Lord Rayleigh's analysis of the gas from the King's Well, at Bath, gave 1·2 part of helium per 1000 volumes, so that it seemed admirably adapted for such experiments. By the kind permission of

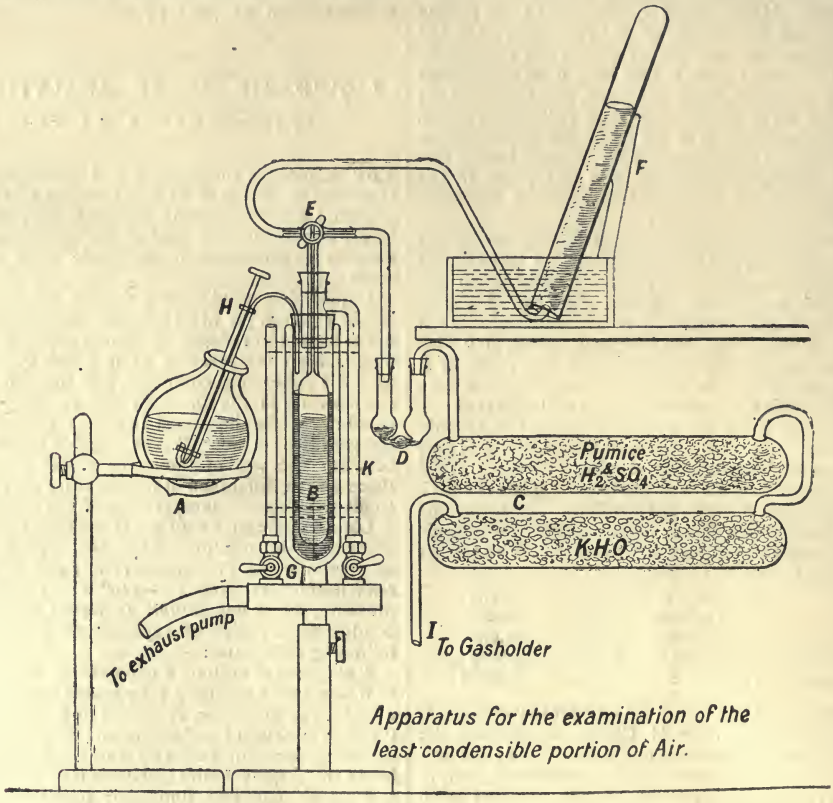


Fig. 1.

* These experiments, along with the succeeding ones on Bath Gas, were all described in a Paper entitled "Liquefaction of Air and the Detection of Impurities," given at the Chemical Society on November 4th, 1897.

the Corporation of Bath, an abundant supply of this gas was obtained for experimental purposes.

In a paper read before the Royal Society on December 19th, 1833 (*Roy. Soc. Proc.*, iii., p. 254), by Dr. Daubeny, Professor of Chemistry at Oxford University, on the "Quantity and Quality of the Thermal Springs of the King's Well in the City of Bath," there are some interesting details. Dr. Daubeny's experiments extended over a month, and he estimated the volume of gas given off as from 80 to 530 cubic inches per minute (average 264). The temperature of the water of the King's Well was 115° Fahr., and the amount of water per minute was equal to 126 gallons. The average volume of gas was 240 cubic inches per minute. The gas was collected from an area of 20 feet in the centre of the bath; the maximum amount of gas obtained was 300 cubic inches, while the minimum quantity was 194 cubic inches per minute. Calculated at the rate of evolution of 250 cubic feet per day for 5000 years, then the whole gas given off amounts to 1456 million cubic feet.

Thirty-two years after Daubeny's experiment Professor Williamson made a more elaborate examination of the Gases of the King's Well. In B.A. Reports, 1865, he gives the following as the volume composition of the gas :—

Carbonic acid.	Oxygen.	Marsh gas.	Nitrogen.
2·948	0·54	0·18	96·33
3·056	0·617	0·216	96·11

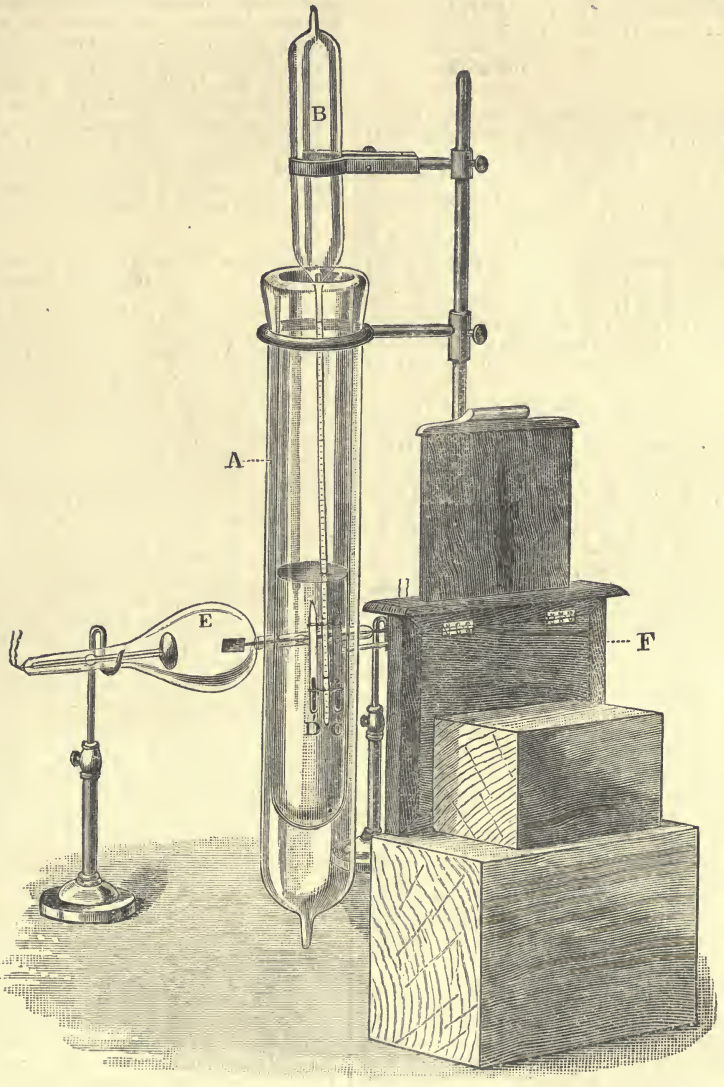


FIG. 2.

A, glass vacuum vessel, containing liquid air. B, tube of argon. C, tube of liquid chlorine. D, tube of metallic sodium. E, Röntgen X ray bulb. F, photographic plate behind sheet aluminium.

Williamson used a funnel 3ft. 9 ins. in diameter to collect the gas, and obtained a quantity equal to a rate of 112 cubic feet per day. This is only about half the amount Daubeny collected, and may be explained by the great alterations made in the bath itself between the dates of the observations.

In passing, it is interesting to note the general character of the saline constituents of the spring, as the most probable hypothesis is that the argon and helium come from the rocks traversed by the water. The following analysis was made by Dr. Attfield:—

	Grs. per gallon.
Carbonate of calcium	7·8402
Sulphate of calcium	94·1080
Nitrate of calcium	0·5623
Carbonate of magnesium ..	0·5611
Chloride of magnesium	15·2433
Chloride of sodium	15·1555
Sulphate of sodium	23·1400
Sulphate of potassium	6·7020
Nitrate of potassium	1·0540
Carbonate of iron	1·2173
Silica	2·7061
	168·2898

Ramsay, the geologist, estimated the mineral ingredients obtained from this source in one year would equal a square column 9 feet in diameter and 140 feet high. Roscoe detected by spectroscopic examination the presence of lithium, strontium, and copper. The sample of Bath gas examined by Rayleigh contained scarcely any oxygen and but little carbonic acid. The weight in a given globe of the N from the Bath gas (2·30522) is about half-way between that of chemical nitrogen (2·299) and "atmospheric" nitrogen (2·3101), suggesting that the proportion of argon is less than in air, instead of greater, as had been expected. Later experiments by Rayleigh proved that this nitrogen contained helium as well as argon.

The sample of gas from the Bath Spring was treated exactly in the same way as the hydrogen mixtures before referred to. During liquefaction there was a marked difference in the appearance of the liquefied gases, for while the hydrogen and air mixtures on condensation gave clear transparent liquids, the product from the Bath gas was turbid, and a precipitate gradually formed which by transmitted light looked yellowish-brown. The yellowish-brown precipitate is a hydrocarbon, probably of the petroleum series, having a marked aromatic smell, and is liquid at the ordinary temperatures. It was probably this gas which Professor Williamson gave as marsh-gas in his analysis. Further research will be made on this substance. Another peculiarity of the liquid nitrogen obtained from Bath gas is that, on examining it with a spectroscope, even through a thickness of 2 inches of liquid, no trace of the characteristic oxygen absorption spectrum could be obtained. In all other attempts to make nitrogen for liquefaction on the large scale, oxygen could always be detected in the liquid by means of its absorption spectrum. Another phenomenon was that the gas from the King's Well could not be entirely condensed by refrigeration with liquid air boiling *in vacuo*. After the cooling had continued for some time, the gas ceased to flow into the condensing vessel, and the upper part of the vessel was occupied by a gas that would not undergo liquefaction at the temperature together with substantially liquid nitrogen saturated with the said gas.

About 70 litres of the Bath gas were condensed, certainly the largest quantity of this gas ever subjected to chemical examination. This was boiled off, and as by accident too much nitrogen had volatilised along with the gas, oxygen was added, and the mixture sparked over alkali, to get rid of the excess of nitrogen. The sample of gas directly collected from the liquid nitrogen contained about 50 per cent of helium. During the sparking the helium lines were well marked (along with others, the origin of which must be settled later), and a vacuum tube filled with the product of the sparking, gave a splendid spectrum of the gas. The recorded unknown lines in the Bath helium were subsequently detected along with helium in the more volatile portion of liquid air (see *Nature*, vol. lviii., p. 570, Letter of Sir William Crookes, Oct. 11, 1898), Eight months after my paper to the Chemical Society, and some two months after this Address was delivered, the same material was found by Professors Ramsay and Travers to exist in argon, and has been recognised and named by them Neon, a new element.

It is therefore possible to separate helium from other gases by liquefaction when it is only present to the extent of 1 part in 1000. From this it would appear that helium is less soluble in liquid nitrogen than hydrogen in liquid air, and is of greater volatility than the constituents of the other gases which were condensed. If the sample of the uncondensed gas from the first liquefaction of the Bath gas were again treated in the same way, a much more concentrated specimen of helium could be obtained. Provided helium were wanted on a large scale, then a liquid air apparatus, similar to that in use at the Royal Institution, transported to Bath, and worked with the gas from the King's Well, could be made to yield a good supply, as the gas contains 1·2 parts in 1000.

Argon, which is present in the proportion of 1·4 per cent, condenses with the nitrogen; but if the liquid be allowed to slowly boil away, a residuum may be obtained containing about 7 per cent of argon. Argon, when frozen, solidifies to a perfectly clear glass.

Absorption of Röntgen Radiation at Low Temperature by Different Bodies.

The transparency of bodies to the Röntgen radiation is an interesting study, although we are not in a position to draw definite conclusions from the results. As a general fact we know the opacity of elements in the solid state increases with the atomic weight.

In the experiments small tubes of the same bore were filled respectively with liquid argon and chlorine, potassium, phosphorus, aluminium, silicon, and sulphur, and exposed at the temperature of liquid air (in order to keep the argon and chlorine solid) in front of a photographic plate shielded with a sheet of aluminium to an X-ray bulb (see Fig. 2). The order of increasing opacity of the shadow of each substance was observed, and the sequence in the list given above represents the results. A tube containing silicon was a little more transparent than the potassium or chlorine. Sodium and liquid oxygen and air, nitrous and nitric oxides, proved much more transparent than chlorine. Tubes of potassium, argon, and liquid chlorine presented no very marked difference of density on the photographic plates.

From these experiments it would appear that argon is relatively more opaque to the X-rays than either oxygen, nitrogen, or sodium, and that it is on a level with potassium, chlorine, phosphorus, aluminium, and sulphur. This may be regarded as supporting the view that the atomic weight of argon is twice its density relative to hydrogen.

(To be continued).

Reductions in the presence of Palladium.—H. Zelinski.—The author has had recourse to reduction in the presence of palladium for transforming the derived iodides and bromides of the cyclic alcohols into carbides: to effect this, zinc turnings are cleaned with alcohol, then with dilute sulphuric acid, and washed with water; the zinc is then placed in water, and a solution of chloride of palladium (1 to 2 per cent) slightly acidulated with hydrochloric acid is added. The zinc becomes coated with a black adherent layer of palladium; the Zn—Pd couple is placed in a flask and partially covered with alcohol; saturated hydrochloric acid at 0° is then added drop by drop. The hydrogen is at first completely absorbed by the palladium, but, when it commences to come off, a reflux condenser is fitted to the flask, and, alternatively, small quantities of alcoholic iodide or bromide, and hydrochloric acid, are added, avoiding violent action. The return is from 70 to 75 per cent.—*Berichte der Deutschen Chemischen Gesellschaft.*

ON THE INJURY TO AGRICULTURAL LAND ON THE COAST OF ESSEX BY THE INUNDATION OF SEA-WATER ON NOVEMBER 29TH, 1897.*

By T. S. DYMOND, F.I.C., and F. HUGHES.

The Inundation of Sea-water.—On November 29th, 1897, owing to an exceptionally high tide, much of the low-lying land round the coast of Essex was flooded with salt water. In some districts the water drained off the land in a few hours, in others several days passed before it was got rid of, while, where the sea-walls were very seriously damaged, several weeks and even months elapsed before this could be done. So difficult did it prove to repair the breaches in the sea-walls in New England and Peewit Island and in part of the parish of Fambridge that the attempt was abandoned, and many hundreds of acres of land have now reverted to the condition of a salting.

Injury to Crops.—The effect of the salt water upon crops existing at the time of the inundation depended upon the nature of the crop and the length of time it was covered with sea-water. Peas and tares were killed in almost all cases; wheat and turnips did not at first appear to be seriously injured when flooded for a short period, but wheat, where flooded for several days, was killed. Nor did the grasses of permanent pasture appear at first to have received any injury (*Note* A). In the course of a few months, however, when active growth began, the more delicate grasses in the pastures died off, and in only one recorded case was a crop growing at the time of the inundation worth harvesting. This was due to injury to the roots. The water of the North Sea contains 2·7 per cent of sodium chloride (common salt) and about 0·5 per cent of other chlorides and sulphates. Of these, the common salt would be present in sufficient quantities to produce plasmolysis of the root hairs (shrinkage of the cell contents) and therefore serious injury to the plant.

Salt Left in the Soil. Is it Injurious to Crops?—The damage done upon agricultural land by sea-water is variously stated to last from five to twenty years. This is usually attributed to the injurious effect of the salt left in the soil upon crops. To ascertain how far this is the case, a determination of the salt was made in samples of soil taken in January, 1898, from different localities and at different depths (*Note* B). Considerable differences are found in the samples, the amount of salt apparently depending on the character of the soil, the length of time flooded, and the rainfall since the water had subsided. On the average it amounted to 0·25 per cent in the top soil, or twenty-five times more than the average amount in the soil from unflooded land. Now, 0·25 per cent in the top six inches of soil is equal to 2½ tons per acre, which if applied as a top dressing might undoubtedly be injurious to many growing crops. But there is evidence that, if diffused through the soil, a much larger percentage of salt might be present without *directly* affecting plant growth (*Note* C). On the island of Wallasea, wheat which had been sown just previous to the inundation and had not then germinated, when examined in February looked well and strong and the root-action was healthy. At Great Wakering, turnips, the rootlets of which were destroyed by the salt water, were found, after two months, to have sent out fresh rootlets just below the crown of the tap-root, which were entirely uninjured by the 0·3 per cent of salt left in the soil. Mustard, turnips, mangolds, beet, cabbages, peas, creeping-bent-grass, and red fescue were sown in flower pots filled with soil from two of the flooded districts; all germinated well, being apparently absolutely uninjured, even at the most critical period of growth, by the salt left in the soil (*Journal of the Essex Technical Laboratories*, 1898, p. 179).

* Read before the British Association (Section B), Dover Meeting, 1899.

Effect on the Condition of the Soil.—But while there was no room for doubt that the salt left in the soil was not sufficient *directly* to injure plant growth, its indirect action in spoiling the condition of the soil was equally serious in its effects, and as a result very few of the crops that promised so well in an early stage of growth were worth harvesting. One of the causes of this was the entire disappearance of earth worms, even in land in which they had previously been abundant. (After the inundation the worms were found strewn upon the ground, and were quickly consumed by seagulls). The use of worms in heavy land in assisting the drainage and thus promoting the aëration of the soil is fully recognised, and their extermination was a serious matter; it is only now, nearly two years after the flood occurred, that young worms are beginning again to make their appearance.

But the injury was more far-reaching than this. For some weeks after the flood occurred, although rather moist owing to the power possessed by sea-salt of absorbing moisture and becoming liquid (*Note* D), the soil was in a remarkably good condition, ploughing well, and forming a capital seed bed; the reason for this being that the immediate effect of salt is to granulate gelatinous clay in the same way that salts of lime are known to do. But this condition gradually altered until the soil became difficult to work and in dry weather hard and "cindery." That the clay had now become far more gelatinous than before was shown by mixing the soil with water and allowing it to settle. While that from the unflooded land settled in a few hours, the soil from the flooded land remained suspended for many weeks. As a result of this change, the drainage of water was very seriously retarded, and it was found by experiment that the rate of percolation of water through the flooded soil was only half as rapid as through the unflooded (*Note* E).

Chemical Changes in the Soil.—In order to learn what was the reason for this change in the condition of the clay, some samples of soil were taken from the flooded and unflooded portions of a field at Burnham and the clay separated from each and analysed (*Note* F). It was found that the amount of lime, magnesia, potash, and soda was less by one-fifth in the clay from the flooded than in that from the unflooded land, while, on the other hand, the combined water in the air-dried clay had increased (*Note* G).

Use of Lime.—It must here be explained that clay as it exists in fertile land consists chemically of silicate of alumina combined with small quantities of the silicates of lime, magnesia, potash, and soda, such double silicates being known as "zeolites," and upon the proportion of these bases the fertility of a soil largely depends. When a clay soil becomes impoverished of lime, the double silicates containing lime are decomposed and the clay is left in a highly gelatinous state, which renders the soil unworkable and drainage defective, the aëration of the soil necessary for healthy development of the roots and nitrification of organic matter being impaired. To ameliorate this condition dressings of lime are employed, which by reproducing the double silicates cause the clay to revert to the granular state.

Now, from the results of analysis it is perfectly clear that the effect of the salt has been to eliminate the lime and other bases from the clay (*Note* H), so that it is to this the bad condition of the soil is due. It follows that, to repair this condition, dressings of lime or weathered gas-lime can be used; for, by giving back the lime to the silicates, such an application will cause the re-granulation of the clay, and therefore restore proper aëration and drainage in the soil. In the case of a soil already rich in lime in the form of chalk stones or shells, the soil will gradually recover its condition without the application of lime, but it is likely that even in this case it will greatly hasten its recovery, the lime being in a more active form.

Importance of Cultivation.—While such a treatment will best secure the permanent improvement of the soil, it must not be forgotten that much may be done towards

securing a good tilth by cultivation; for, given favourable weather, even gelatinous clay may be dried and rendered temporarily friable by thorough aëration. An examination of the produce of crops on the flooded land (given in the schedule) will show that far and away the best results in 1899 were obtained by fallowing and frequent ploughing in 1898. Anything that assists the opening, aëration, and drainage must be beneficial on the flooded land. At Great Wakering, the effect on a crop of turnip seed of—(1) farmyard manure, (2) sewage cake, and (3) long hay manure (obtained from vessels carrying cattle) were compared. As might be expected, the best crop was obtained with the long hay manure and the worst with the sewage cake; the former having best promoted the aëration and drainage of the soil. Hence ploughing in long dung, spoilt hay, and even a white straw crop that is not worth harvesting, should prove most useful.

Elimination of Salt.— And by promoting drainage a further purpose is best served—the elimination of the salt. It is a mistake to suppose the salt will be appreciably diminished by the growth of crops. Even mangolds, which absorb more salt than any other farm crop, would only remove 136 lbs. per acre, whereas the salt in the first 9 inches (if 0·1 per cent) amounts to 3000 lbs. (*Note* I). Hence it is only by taking advantage of the rainfall and encouraging rapid drainage that the salt can be eliminated. Salt is, of course, very soluble in water, and, unlike some other soil constituents, is not retained by the soil but is always found in drainage water. From an experiment made in the laboratory, it was found that 1¾ inches of rain water, when allowed to filter through 6 inches of the soil from the flooded arable land at Wallasea was more than sufficient to remove almost every trace of salt. In the field, however, it must be remembered that while, during wet weather, salt is washed downwards, during dry weather, owing to evaporation of water from the surface of the soil, there is a movement of salt upwards, so that the complete elimination of the salt would require a much greater rainfall than the foregoing experiment indicated. The total rainfall for the eighteen months from December 1st, 1897, to May 31st, 1899, was 26¾ inches (*Note* K), and to ascertain how far this had washed the salt from the flooded land a second series of determinations was made last June. It was found that in almost every case the salt had been very materially reduced, in some instances to one-tenth, and on the average to one-quarter, of the amount present in the beginning of 1898. This must be considered a satisfactory result, and if care is taken to keep the drains open and to run off the salt water as it collects in the dykes, a reasonably heavy rainfall during the coming winter should effectually remove the remaining salt (*Note* L).

Impoverishment of the Soil.—It has already been pointed out that the chemical action of the salt upon the clay of the flooded soils has resulted in the elimination of a part of the lime, magnesia, potash, and soda, which have been converted from the form of insoluble silicates into soluble muriates. The effect of the inundation was, therefore, greatly to increase the supply of available plant food. That this was the case was shown by a determination of the *available* constituents in the Burnham soil (*Note* M), the clay of which had been previously analysed for the *total* constituents. It was found, for example, that while the total potash in the clay had been reduced from 1·12 to 0·84 per cent by the action of the salt, the soluble or available potash in the whole soil was increased from 0·025 to 0·079 per cent, and not only the available bases, but the available phosphates also had been increased in quantity. But while the rendering soluble of these constituents has increased the available plant food, it must also have given rise to considerable loss by drainage, so that the total quantity of the constituents has been reduced.

Artificial Manures.—It is therefore clear that the effect of the inundation has been very materially to impoverish the land, but that owing to the large increase in the availability of the remaining constituents, there is abundant mineral plant food for the immediate needs of crops, and that, therefore, potash and phosphatic manures are likely for some time to come to prove less beneficial than upon land that has not been flooded. This remark does not apply to nitrogen; for, owing to the inefficient aëration of the soil, the production of nitrate must have been retarded, and in the event of the soil being in such a condition as to allow a luxuriant crop, a dressing of nitrate of soda should prove useful for cereal and root crops, and especially permanent pasture. For crops upon which phosphatic manures are specially required, basic slag should be used in preference to superphosphate, both because the salt still present possesses a solvent action for the slag, and because the lime of the slag is itself useful—the acid of superphosphate injurious—to the condition of the clay.

Crops.—With regard to the crops best adapted to cultivation on the flooded land, much information may be gained from the experience of farmers during the past two years tabulated in the schedule (*Note* N). It is clear that success depends more on the condition of the land than upon the particular crop selected for cultivation. Wheat, barley, oats, and mangolds have all given a fair yield in some cases, and in others have entirely failed. Rye-grass, however, which was expected to answer, even if other crops did not, has in some cases failed to germinate, and in all proved disappointing, and instead a rank growth of twitch and squirrel-tailed grass and other weeds has appeared. But there is one class of crops which has proved almost uniformly successful, namely, the *cruciferous*. At Mundon, on the flooded land, a larger crop of kale was obtained in the autumn of 1898 than had ever been given on the farm before; on the enclosure at Tillingham, where all the crops had failed, rape, among other self-sown plants, was growing strong and vigorous in the spring of 1899; at Burnham, on land sown with rye-grass, the soil last winter became smothered with charlock; on Foulness, mustard gave a good half crop in 1898, and at Dengie nearly an average crop in 1899; while at Wakering, turnip seed sown in 1897 gave a good half crop in the spring of 1898, and was the only recorded case of a crop which, submerged by the salt water, was worth harvesting. There can be little doubt that, on land where other crops fail, one or other of the cruciferous crops will be found to succeed.

In conclusion, we wish to express our indebtedness and hearty gratitude to Messrs. E. A. Fitch, J. Grainger, J. C. Chillingworth, Wm. Sewell, E. J. Smith, A. B. Croxon, A. W. Croxon, E. A. Wedd, S. W. Squier, A. M. Clarke, W. H. Vellacott, G. H. Cross, F. D. Girling, P. Stanford, and other gentlemen for the help and information they have afforded and which has enabled us to prepare this report.

NOTES:

A. According to Longfellow, the French farmers of Nova Scotia purposely allowed their meadows to be periodically flooded with salt water:—

> "Dikes that the hands of the farmers had raised with labour incessant
> Shut out the turbulent tides; but at stated seasons the floodgates
> Opened, and welcomed the sea to wander at will o'er the meadows."—*Evangeline.*

Arthur Young, in his "General View of the Agriculture of Essex" (p. 13) published in 1813, states that "forty years ago the whole of one of the islands on the Essex coast was under water and no corn got for two years; but after that much greater than ever, so as to furnish an effectual proof that (salt) water did good, after being chastened and corrected by the atmosphere."

B. The soils of Foulness, Great Wakering, and Tillingham are heavy alluvial soils overlying sand, the last-

mentioned being distinguished by a layer of sea-weed (¼th inch) separating the top soil from the sandy subsoil. Those at Northey Island, Burnham, and Wallasea are heavy soils on a clay subsoil. At West Thurrock the soil is a deep heavy alluvial soil overlying peat; the land is not drained. The first series of samples, with the exception of that from Great Wakering, were taken for analysis in January, 1898, and it is noticeable that the rainfall since November, 1897, had been even then sufficient to wash most of the salt into the subsoil, except in the case of West Thurrock, where the land was flooded for eight weeks, and no rain had occurred after the salt water had drained off before the samples were taken. At Great Wakering, the samples were taken a month later, and the salt had, by evaporation of water, been again carried upwards. The second series of samples were taken in May, 1899.

C. Interesting facts upon this subject were deduced during the reclamation of Lake Aboukir in Egypt (*Minutes of the Proceedings of the Institute of Civil Engineers*, 1890, ci., pp. 189—204). This lake had an area of 30,000 acres, and was 3¼ feet below sea-level. It is known to have been flooded with sea-water in 1715. Since then it has been flooded by the Nile each year in winter and evaporated every summer, a deposit of pure white salt, 3 or 4 inches in thickness being deposited in the depressions. The soil from the bed of the lake was found by Dr. Voelcker to contain from 8 to 9 per cent of sodium chloride, and to reclaim it, 450 tons of salt had to be extracted from each acre. The methods adopted in Egypt to reclaim salt land are—(1) By warping until a sufficient depth of silt is produced to grow crops; (2) by washing *up* the salt by continuously passing fresh water over the land; (3) by washing the salt *down*, the land being flooded with fresh water and dykes cut, into which the water drains through the soil. The last method was adopted in the case of Lake Aboukir, and after one year's washing, the salt was reduced to 0·5—2 per cent at a depth of 12 inches. It was found that when the soil contained 2 per cent of salt, crops of annual grasses grew 2 feet in height, and when further reduced to 1 per cent full crops, 4 feet high, were obtained. When the salt was reduced to 0·5 per cent good crops of rice and clover could be grown. The fertile soil in the neighbourhood contains 0·01 per cent of salt. Upon the higher portion of the bed of the lake, the soil contained 1·6 per cent of salt before reclamation, and upon these, scrubby crops of barley were annually grown.

D. This is due to the chlorides of magnesium and calcium which are contained in sea-water in small quantities; chloride of sodium is not itself deliquescent.

E. This was determined by filling two percolators with the soils and, after saturating with water, noting the time taken for each c.c. of water to percolate through :—

	Flooded.	Not flooded.
First c.c. of water occupied	16 minutes	8·3 minutes.
Second " "	15·8 "	8·4 "
Third " "	16·2 "	8·4 "
Fourth " "	16·7 "	8·5 "
Fifth " "	16·9 "	8·6 "
Sixth " "	16·7 "	8·6 "
Seventh " "	17·4 "	8·7 "
Mean	16·5 "	8·5 "

An experiment was also made on the retentivity of the soil for water. It was found that 100 grms. of the air-dried soil from the—

	Expt. 1.	Expt. 2.	Mean.	
Flooded land retained	40·6	42·0	41·3	grms. of water
Unflooded " "	41·7	42·7	42·2	" "

so that the water capacity of the soil had not been greatly altered.

F. For this purpose the samples of soil were mixed with water in a cylinder, and the fine clay removed by a slow stream of water into a large trough, where it was allowed to deposit. The clay thus obtained was exposed to a current of dry air until it ceased to lose weight. The results of analysis were as follows :—

	Clay from flooded land. Per cent.	Clay from unflooded land. Per cent.
Lime	1·23	1·42
Magnesia	1·16	1·54
Potash	0·84	1·12
Soda	0·25	0·37
Phosphoric acid	0·21	0·16
Insoluble sand and clay ..	62·77	61·10

To determine the water of hydration, the air-dried clay was heated to 240° C., the highest temperature at which it could be safely heated without decomposing any organic matter present :—

	Clay from flooded land. Per cent.	Clay from unflooded land. Per cent.
Loss at 240°	7·38	5·34
Further loss on ignition ..	9·48	9·62
Total loss on ignition ..	16·86	14·96

G. It is remarkable that since the inundation occurred, the land frequently becomes coated with a white efflorescence of gypsum (sulphate of lime), no doubt partly produced by reaction of the liberated lime with the sulphates of the sea-water.

H. Professor Way and others have shown that when solution of common salt acts upon zeolites, lime, magnesia, and potash are eliminated, their place being taken by an equivalent quantity of soda. In the case of the flooded land this may very probably have been the first change, especially because it is a substitution which need not alter the physical condition of the clay, and it was observed that the soil worked well for some months after the inundation occurred. But a further change has taken place during the eighteen months that elapsed before the samples were taken—a change which rendered the clay gelatinous and unworkable, and by which the soda has itself been eliminated, it is to be supposed, as carbonate. Gelatinous clay, it is probable, differs from granular clay in consisting of far smaller particles; it is, in fact, colloidal, and this is shown by the permanent suspension of such clay when mixed with water. If a base be removed from an aggregation of molecules to which it is essential, the aggregation will be broken down into, at any rate, smaller aggregations, so that the elimination of the soda would have the observed effect of rendering the clay gelatinous. If in the reaction the soda in the double silicates is replaced by water, this might partly account for the greater loss in weight of the dry gelatinous clay when heated to 240° C. than of the dry granular clay.

I. The principal farm crops absorb on the average the following quantities of salt per acre :—

	Pounds.		Pounds.
Wheat	4	Red clover ..	16
Barley	7	Meadow grass ..	24
Potatoes	7	Swedes	25
Beans	9	Mangolds	136
Oats	10		

K. The monthly rainfall for the eighteen months from December, 1st, 1897, to May 31st, 1899, as observed at Chelmsford was as follows :—

December, 1897 ..	2·02	September, 1898 ..	0·29
January, 1898.. ..	0·74	October ,, ..	2·32
February ,, ...	0·80	November ,, ..	2·03
March ,, ...	1·38	December ,, ..	2·30
April ,, ...	1·15	January, 1899.. ..	1·81
May ,, ...	1·95	February ,, ...	1·60
June ,, ...	2·21	March ,, ...	0·79
July ,, ...	0·64	April ,, ...	2·32
August ,, ...	0·86	May ,, ...	1·50

L. At Foulness, although the subsoil is sandy and the drainage free, only a small reduction in the amount of salt has taken place. It is to be suspected that this is due to the salt water being allowed to remain in the dykes, so that in dry weather it has been re-absorbed by the soil. The field on Northey Island is a sloping one, and the subsoil is heavy clay; the salt would therefore be washed from the upper part of the field to the lower part from which the sample was taken, so that a material decrease of the salt could not be expected. In this case water furrows should be cut across the field. In the preliminary report it was suggested that until the salt was washed from the surface soil, ploughing should be avoided. As this suggestion has been very strongly criticised, it should be pointed out that the same principle is involved as in the deep cultivation *versus* the deep ploughing of land overlying yellow clay. The object was to prevent the salt from being brought again to the surface. The first object, it was suggested, should be to eliminate the salt, the second to produce a good tilth; but even in February, 1898, the salt was sufficiently washed into the subsoil in most cases for ploughing to be carried on without bringing up much salt to the surface.

M. The available soil constituents were determined by Dyer's method by extracting with a 1 per cent solution of citric acid. The results were as follows:—

	Soil from flooded land. Per cent.	Soil from unflooded land. Per cent.
Lime	0·695	0·791
Magnesia	0·101	0·036
Potash	0·079	0·025
Soda	0·069	0·013
Oxide of iron and alumina .	0·933	0·777
Phosphoric acid	0·040	0·029
Silica	0·300	0·77

N. Some information respecting the crops that can be best grown on land containing salt may be gleaned from the experience of those who have reclaimed land on the coast. A new enclosure at Tillingham was made in 1871. It was flooded again in 1874. In 1881 a portion of the land was broken up and sown with oats, but these came to nothing and were fed off. In 1882 oats produced a crop of about six quarters an acre, but very light in weight. In 1883 oats did about the same; mustard produced a very light crop. In 1884, wheat gave about three quarters an acre. In 1885, oats gave six quarters. In 1886, wheat, barley, and beans each did fairly well, and the land has been successfully cropped till again flooded in 1897. A new enclosure at Holderness at the mouth of the Humber was reclaimed with much less difficulty. A good growth of grass and abundance of white clover spontaneously appeared in this case within three years of enclosure. On the part of the enclosure intended for arable land, rape was sown the third and fourth years after enclosure, and gave an exceptionally good yield; oats and beans were successfully grown the next season, and wheat the season after (*Minutes of Proceedings of the Inst. of Civil Engineers*, xxi., p. 454). We are informed by Mr. I. J. G. Kakebeeke, of Goes, Holland, that in the case of some land recently flooded with salt water in his neighbourhood, red clover was found to be the most remunerative crop.

COMPARATIVE ACCURACY OF TITRIMETRIC AND GASOMETIC METHODS OF ESTIMATING HYDROGEN DIOXIDE IN PRESENCE OF VARIOUS PRESERVATIVE AGENTS.*

By CARL E. SMITH.

The method of estimating hydrogen dioxide most extensively used is that of titration with potassium permanganate. Besides being more readily applied than any other, this method has always been presumed to give accurate results, at least sufficiently so for all practical purposes. Dr. Charles Rice, however, has observed that its accuracy is affected by the presence of glycerin, which some manufacturers add to the solutions to give them stability. A variety of other substances have from time to time been reported to be in use for the same purpose, and it was suspected that at least a part of them might also exert an influence on the results of the method. Such substances are boroglycerin, boric, salicylic, and benzoic acids, acetanilide, salol, &c. It was important, therefore, to know if the inaccuracies introduced by the presence of glycerin or any other of the above enumerated substances are so great as to make the method worthless, and, if so, whether a method could be found that is not affected by these additions, one that could be relied upon under any conditions likely to occur in the assay of commercial solutions of hydrogen dioxide. It was the writer's task, for this purpose, to make comparisons of the more prominent titrimetric and gasometric methods under such conditions as might be encountered in practice. The experiments were confined to four methods, a description of which will first be given.

Titrimetric Permanganate Method.—When a solution of potassium permanganate is gradually added, with agitation, to a solution of hydrogen dioxide containing sulphuric acid, the permanganate is decolourised through the formation of manganous sulphate, and all available oxygen is liberated from the hydrogen dioxide, together with an equal amount from the permanganate. When the last drop of the solution added leaves a permanent red colour after agitation, the reaction is ended. It proceeds in accordance with the following equation:—

$$5H_2O_2+2KMnO_4+3H_2SO_4= =5O_2+2MnSO_4+K_2SO_4+8H_2O.$$

If 1 c.c. of hydrogen dioxide solution is taken and a N/10 solution of permanganate used, the number of cubic centimetres requred to produce a permanent red colour, multiplied by 0·56, will indicate the number of volumes of available oxygen yielded by one volume of the sample.

Gasometric Permanganate Method.—The reaction made use of in this method is the same as in the preceding one, the principal difference being in the direct measurement of the liberated oxygen instead of its calculation from the amount of permanganate consumed. The operation is performed in a gasometer, or nitrometer, several forms of which have been devised. A description of the form best suited to this work and its use will be found in the Appendix of the *U. S. P.* of 1890, under "Gasometric Estimations," and in the Dispensatories. The writer operated in the following manner:—The measuring tube, graduated to 100 c.c., is filled with a saturated solution of sodium chloride, 2 c.c. of the sample are accurately measured into the funnel tube and slowly let into the measuring tube, care being taken that no air is admitted. Ten c.c. of 10 per cent sulphuric acid are then admitted in the same manner, and finally 20 c.c. of a 2 per cent solution of potassium permanganate. When the reaction has nearly ceased, the tube is inverted a few times to in-

* Report from Research Committee D, Section II., of the Committee of Revision of the U.S. Pharmacopœia. From the *American Journal of Pharmacy*.

sure complete decomposition of the hydrogen dioxide. This must be repeated several times within the next five minutes, on account of the voluminous precipitate of hydrated manganese dioxide, which prevents small bubbles of gas from rising to the top. The tube is then placed in a vertical position, and, when the volume of gas becomes constant, the liquid in the equilibrium tube is adjusted to the same level as that in the measuring-tube. The volume of gas is then read and the temperature noted. Since the standard of strength of hydrogen dioxide solutions is *not* based on the volumes of oxygen yielded at ordinary room temperarure, but on the volume the gas would occupy at 0° C. and 760 m.m. barometric pressure, a correction is required for accurate determinations. The writer made correction for variation in temperature only, as sufficient for ordinary purposes. The reader is referred to the "Pharmacopœia" for the formula and tables required for this. It should not be omitted, as the error would be quite considerable. A solution yielding 10 volumes of oxygen at 0° C., would yield 10·55 volumes at 15°, 10·75 volumes at 20°, 10·9 volumes at 25°, &c.

In the writer's hands this method does not give very encouraging results. Duplicate estimations differ much more than with other methods, the precipitated manganese dioxide collects near the top of the liquid, and makes a close reading of the volume impracticable, besides obstructing the passage of gas bubbles. While not entirely worthless, it is much less satisfactory than the following method.

Gasometric Hypochlorite Method.—This method is recommended by D. B. Dott (*Ph. J. Tr.*, 1890, p. 833), who uses a solution of ordinary bleaching powder, also filling the apparatus with it instead of sodium chloride solution. Mr. Dott obtains appreciably higher results than by titrimetric methods, and concludes the method to be more accurate than the latter. The reaction is analogous to that of the permanganate methods, as follows:—

$$Ca(ClO)_2+2H_2O_2=2O_2+CaCl_2+2H_2O.$$

In some of the present writer's experiments a solution of chlorinated soda of approximately U.S.P. strength was used, in others a solution of chlorinated lime containing about 4 per cent of available chlorine. Preference is given to the latter, as with the other a white flocculent precipitate (probably sodium hydrate and carbonate) is formed, which is open to the same objections as that incidental to the permanganate method. A saturated solution of sodium chloride was used in all cases for filling the gasometer. Two c.c. of the sample are admitted into the measuring tube, the funnel tube rinsed with a little water; this also let in, and then 20 c.c. of the chlorinated lime solution added. From this point the procedure is the same as explained under the permanganate method.

With solutions containing in addition to hydrogen dioxide only small quantities of mineral acids and alkali salts, quite satisfactory results were obtained by this method; but in the cases of solutions to which any of the various preservatives had been added, there was a decided tendency, almost throughout, toward too low results. No appreciable error seems to be introduced through the solubility of oxygen in the liquid, above which the gas is collected, as no higher results were obtained when the liquid had previously been saturated with oxygen.

(To be continued).

Truro Sewage Scheme.—The Corporation of this city have unanimously agreed to consult Mr. Candy, of the International Purification Syndicate, 109, Victoria Street, Westminster, with regard to the treatment of the sewage of Truro upon the system of purification by Bacteria beds, which dispenses with the necessity of septic tanks and coke filters.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 14, October 2, 1899.

Two Chlorobromides of Tungsten.—Ed. Defaçoz.—The author finds that it is not possible to prepare hexabromide of tungsten by the action of liquid hydrobromic acid on the hexachloride in sealed tubes kept at a temperature of 70°, but he has prepared two chlorobromides: one, the more stable of the two, is formed at about 70°, and is the hexachloro-trihexabromide, $WCl_6.3WBr_6$; the other is obtained at a temperature of 15°, and is the hexachlorobromide, $WCl_6.WBr_6$. These two compounds are the first known chlorobromides of tungsten. The former substance is green, and composed of a mass of small crystals which melt at 232°; on exposure to air, it rapidly alters, turning brown in colour.

Hypophosphite of Copper and its Decomposition by Precipitated Palladium.—R. Engel.—The author has succeeded in preparing copper hypophosphite, a substance which hitherto had not been obtained owing to the facility with which hypophosphorous acid reduces copper salts. The preparation consists in precipitating a solution of copper sulphate by the molecular equivalent of a solution of hypophosphite of barium. The precipitated sulphate of barium can be filtered off, and the solution can be evaporated in air over sulphuric acid. The solid salt is white, and when anhydrous has the formula $(PO_2H_2)_2Cu$. Precipitated palladium decomposes copper hypophosphite in the cold, metallic copper being deposited and hydrogen evolved. The reaction is represented by the equation $(PO_2H_2)_2Cu+2H_2O=Cu+2PO_3H_3+H_4$.

Salicylic and Para-oxybenzoic Aldehydes and Salicylhydramide.—MM. Delépine and Rivals.—During the thermo-chemical investigation of the derivatives of salicylic aldehyde, the authors have obtained results incompatible with previous determinations. Therefore they have measured again the heat of formation of salicylic acid and aldehyde, besides that of paraoxybenzoic aldehyde, of salicylhydramide, with many control experiments.

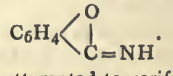
Berichte der Deutschen Chemischen Gesellschaft. December 12, 1898.

On the Compounds of Carbonic Acid with Water, Oxide of Ethyl, and the Alcohols.—W. Hempel and J. Seidel.—A compound of carbonic acid and water, having for its formula CO_2+8H_2O, has already been described. This compound may be obtained by placing a certain quantity of water in a thick tube, cooling to −80°, and adding carbonic acid snow; the tube is then sealed up and allowed to return to the ordinary temperature. We notice that the contents of the tube separate into two liquid layers, the water below and the carbonic anhydride above. At the same time crystals having the above-mentioned formula are deposited; these melt at 8° at a pressure of 43 atmosperes, and decompose between −2° and +20° at the normal pressure. Carbonic acid snow also dissolves in ether; if it is added to water saturated with ether a white precipitate is obtained; the composition of this substance is variable and depends on the temperature of the mixture. At −50° it is represented by the formula $(C_2H_5)_2O+CO_2+4H_2O$. Liquid carbonic acid unites with the alcohols, giving compounds fusible above the freezing-point of alcohol. Thus the compound—

$$CO<^{OH}_{OCH_3}$$

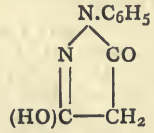
solidifies at −79° and melts at −60°: ethylic ether, $C_2H_6O+CO_2$ melts at about −61°, and amylic ether at −56°.

The Constitution and Cryoscopic Constants of *o*-Cyanophenol.—K. Auwers and A. J. Walker.—The phenols generally behave in an abnormal manner from the cryoscopic point of view when benzene is used as a solvent; *o*-cyanophenol, on the contrary, is again abnormal and behaves like the para-isomer. Thus it is supposed that it may have the following constitution :—



The authors have attempted to verify this hypothesis experimentally, and have found that *o*-cyanophenol does not exist in two tautomeric forms, and does not give rise to two series of derivatives. They have also studied a series of substitution derivatives of *o*-cyanophenol from the cryoscopic point of view, the results of which are fully described in this paper.

On Phenyl-1-hydroxy-3-pyrazolone-5.—A. Michaelis and H. Rœhmer.—The present memoir has for its object the completion of the study of phenylmethylpyrazolidone, and to show that the formula attributed to it should be by preference that of an oxypyrazolone :—



To prepare this body, 1 molecule of chloromalonic ether is mixed with 3 molecules of phenylhydrazin, and allowed to stand for three days, while preventing the access of air. The mass is then dissolved in soda, the solution is washed with ether, then supersaturated in the cold with hydrochloric acid. The yellow precipitate which is formed is drained, washed with water, and re-crystallised in alcohol; we thus obtain bright yellow flakes fusible at 192°. The original oxypyrazolone unites directly with benzoïc aldehyde at 130°, giving a benzylidenic compound, which crystallises in reddish needles fusible at 108—109°, and soluble in the usual solvents. If phenyloxypyrazolone (1 mol.) is heated with oxychloride of phosphorus (2 mols.) in a closed vessel to 150° for six hours, it is transformed into phenyl-1-dichloro-3.5 pyrazol, which is purified by a current of steam. This body boils at 170—172° at 16 m.m., and crystallises on cooling in white needles fusible at 25—26°.

Transformation of Geraniol into Methylheptenol.—F. Tiemann.—M. Barbier has, by acting under pressure with alcoholic potash on geraniol, obtained an alcohol boiling at 79° at 10 m.m., to which he gave the name dimethylheptenol. The author shows that this alcohol is identical with the methylheptenol obtained by acting with potash on methylheptenone. The identification was made by means of the physical and chemical properties of the two products. The action of alcoholic potash on linalool under pressure does not give rise to any analogous product.

On Citral (Geraniol) and Essence of Lemon-grass.—F. W. Semmler.—A controversial article on the subject of the identity of citral and the aldehydes obtained from essence of lemon-grass.

January 9, 1899.

Influence of the Formation of Salts on the Saponification of the Amides and Ethers by means of Alkalis.—E. Fischer.—Already inserted.

The Formation of Putrescine from Ornithine.—A. Ellinger.—Ornithine was obtained by Jaffe's method, by hydrating its benzoyl derivative, ornithuric acid, by means of hydrochloric acid. The hydrochlorate of ornithine was dissolved in water, and soda added until slightly alkaline. On infecting this with a little putrid pancreas, and keeping at 30° for three days, CO_2 is given off, and trimethylene diamine can be obtained from the liquid. This is characterised by its transformation into a benzoylised and chloroplatinate derivative. Ornithine has the following constitution :—

$$CH_2(NH_2)—CH_2—CH_2—CH(NH_2)—CO_2H.$$

On the Identity of α-Digallic Acid and Tannin.—P. Walden.—Already inserted.

On the Isomeric Benzoylketoximes.—J. Schmidt.—Already inserted.

On the Non-nitrated Products of the Decomposition of Morphine.—E. Vongerichten.—In this paper the author establishes the relations which exist between morphenol and morphol; methylmorphenol, reduced by sodium and absolute alcohol, gives a crystalline phenol easily oxidisable, and which gives an oily acetylised derivative. Now the oxidation of this latter by chromic acid, in acetic solution, leads to a quinone identical with methylacetylmorpholquinone. Morphenol, distilled with zinc powder, gives 50 per cent of phenanthrene.

MEETINGS FOR THE WEEK.

FRIDAY, 27th.—Physical, 5. "Magnetic Properties of the Alloys of Iron and Aluminium," by Dr. S. W. Richardson. Exhibition of a Model illustrating a number of the Actions in the Flow of an Electric Current, by G. L. Addenbrooke. Repetition of some Experiments with the Wehnelt Interrupter devised by Prof. Lecher, by W. Watson.

SECOND EDITION, 8vo, 9s.

OUTLINES OF THEORETICAL CHEMISTRY.

By LOTHAR MEYER,

Professor of Chemistry in the University of Tübingen.

Translated by P. PHILLIPS BEDSON, M.A. (Dun.), D.Sc. (Lond. et Dun.), B.Sc. (Vic.), F.I.C., F.C.S., Professor of Chemistry in the Durham College of Science, Newcastle-upon-Tyne; and W. CARLETON WILLIAMS, B.Sc., F.I.C., F.C.S., Professor of Chemistry in the University College, Sheffield.

With a Preface by the Author.

*** *In preparing a second edition of the translation of Meyer's "Outlines of Theoretical Chemistry," the translators have availed themselves of the second edition of the German, published in* 1893, *a few years before the death of Lothar Meyer. Whilst the original form has been still retained, they have, by occasional footnotes and appendices, sought to bring the book up to date.*

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Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V.

UNIVERSITY COLLEGE, LONDON.

THE MANIPULATION OF GASES.

By MORRIS W. TRAVERS, D.Sc.

A Course of SIX LECTURES will commence on FRIDAY, NOVEMBER 10th, at 5.30 o'clock.

Syllabus on application to the SECRETARY, University College, London, Gower Street, W.C.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E, M.S.C.I.,

Fellow of the Chartered Institute of Patent Agents,

NORFOLK HOUSE, NORFOLK STREET, LONDON, W.C.

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THE CHEMICAL NEWS.

Vol. LXXX., No. 2083.

EVOLUTION OF CHEMISTRY IN THE LAST TWENTY YEARS.*

By Dr. A. LADENBURG.

When we look back upon the development of chemistry during the last fifteen or twenty years, we find that it is distinguished by the constantly increasing prominence of physical or, as many call it, general, chemistry, which from small beginnings has advanced to the position of a science of the first rank. Contributions to this end have, naturally, been made in particular by eminent scientists such as Horstmann, Gibbs, and van 't Hoff, who have devoted themselves to this department exclusively, and, by their ideas and discoveries, have brought about its advancement. On the other hand, however, it cannot be denied that this advancement does not coincide fortuitously with the appearance of Ostwald's great Textbook of General Chemistry, but that the latter, in which the attempt is for the first time successfully made to give a complete representation of what has been accomplished up to the present in this department, aroused and stimulated the tendency towards investigation in an altogether exceptional manner. Further, the establishment by Ostwald and van 't Hoff of the *Zeitschrift fur Physikalische Chemie*, in which all the more important investigators in this department are active as collaborators, has done a great deal to advance the subject; so that this publication must be placed side by side with the best journals representing our science and be looked upon as of equal value with them.

In now passing on to the subject itself, I begin, in the first place, with the law of mass action, which is apparently destined to play a constantly increasing part.

These chemical studies received a new direction and a fresh stimulus from the theory of phases, due to Gibbs. The phase rule developed by him, and proved both by him and afterwards by van der Waals, is to the following effect:—Complete equilibrium can only exist when the number of phases present exceeds the number of components by one. By phases, are understood homogeneous portions of a system. Each state of aggregation represents at least one phase. In the solid or the liquid state two or more different phases may exist; a gas, however complex, can only form one phase. Complete equilibrium is a condition which depends *only* on the temperature, and is mostly definable by a certain value of the pressure. By components are understood all those chemical elements taking part in the equilibrium, whose quantities are subject to independent variation. Ammonium chloride, for example, has only one component, it being a matter of indifference whether we choose nitrogen, hydrogen, or chlorine. If excess of ammonia or of hydrochloric acid is added, there are then two independent components. Calcium carbonate, above its dissociation temperature, has two independent components, calcium and carbon; for the composition of the solid phases—calcium carbonate and calcium oxide—cannot be determined by the amount of calcium alone. Hence complete heterogeneous equilibrium is established in the case of ammonium chloride with two phases, and in the case of calcium carbonate with three phases.

If there are $n + 2$ phases and only n components, equilibrium is only possible at singular points; that is to say, at some definite temperature (multiple point, inversion or transformation temperature). If there are just as many phases as there are components, the equilibrium is incomplete; that is, to each temperature there corresponds a series of pressures.

This phase rule has received numerous practical applications, the work of Roozeboom deserving especial mention. Roozeboom studied the connection of the states of aggregation, the equilibrium between water and sulphurous anhydride, the hydrates of ferric chloride, &c. The phase rule can also be applied to dissociation phenomena, to the reciprocal transformation of allotropic modifications of elements, and so forth.

More important perhaps than the phase rule (the significance of which is exaggerated by many, seeing that it merely furnishes a plan for the exposition of heterogeneous equilibrium) is van 't Hoff's theory of solution. The conception that forms the foundation of this theory is based upon the well-known experiments of Pfeffer, which only became possible after the discovery by Traube of semi-permeable membranes.

In explaining osmotic pressure as the result of the impacts of the dissolved molecules upon the walls of the vessel, van 't Hoff arrives at a comparison between substances in the dissolved condition and in the state of gas. The laws of Boyle, Mariotte, and of Henry Gay-Lussac, as well as the fundamental hypothesis of Avogadro, can now be applied directly to solutions; so that this branch, which has hitherto been one of the most obscure in the whole subject of chemistry, at once becomes fully accessible to investigation. As a consequence, important results, which are capable of being turned to account throughout the whole range of chemistry, are immediately obtained.

The important relations subsisting between the depression of freezing point, the diminution of vapour pressure, and the elevation of boiling point on the one hand, and the molecular weight of the dissolved substance on the other (which were ascertained experimentally and formulated by Raoult in particular), now attain their theoretical significance for the first time. As the outcome of this, and also in consequence of improvements and simplifications that Raoult's methods of molecular weight determination underwent, these methods very soon obtained a footing; and their results, especially those from the depression of the freezing point, are considered to be just as accurate as those from the vapour density.

Raoult had already pointed out, however, that aqueous solutions of salts of bases and of acids, in particular, did not agree with his rules; but always yielded results that were too low, and only attained to a value from one-half to one-third of that which had to be regarded as the normal number. All explanation of this anomaly was at first wanting, so that the general applicability of van 't Hoff's theory appeared to be placed in doubt. The difficulty was got rid of in the same way as in the case of the abnormal vapour densities.

Arrhenius proceeded in this matter in exactly the same way that Cannizzaro, Kekulé, and Kopp had previously solved the other difficulty. His theory, advanced in 1887, adopts as actually existent that condition which must be assumed to exist in order to arrive at an agreement between the theory of van 't Hoff and the numbers furnished by Raoult's rules. He draws attention to the fact that it is in the cases of solutions of those substances which are electrolytes and break up, under the influence of the electrical current, into their ions, that numbers are obtained which do not agree with theory. He now assumes that the ionisation does not merely take place as a result of the passage of the current, but that it occurs during the dissolution; and that the latter is thus accompanied by a more or less complete (electrolytic) dissociation, the extent of which depends principally upon the degree of dilution. A number of methods for determining the extent of this dissociation very soon presented themselves, as was pointed out by Arrhenius himself, but

* Read before the British Association (Section B), Dover Meeting, 1899.

also by Planck, Ostwald, and others; and (what is very important) these methods give results that agree with one another.

The hypothesis of Arrhenius found a great many opponents—indeed it could hardly have been expected that it would be otherwise. The assumption that an aqueous solution of common salt contains free sodium and chlorine ions (which, however, are nothing but electrically charged atoms that behave like free molecules) was certain to meet with opposition from chemists, since it stood in contradiction to observation and thus included something of a metaphysical nature. Besides, the explanation of many reactions that had formerly appeared simple was rendered much more difficult; as, for example, the decomposition of water by the alkali metals, since in this reaction no combination with oxygen and, on the other hand, no displacement of hydrogen ions by sodium ions, could be assumed. But of what consequence are considerations of this kind in face of the great advantages which the theory of electrolytic dissociation affords? A large number of otherwise inexplicable facts are satisfactorily explained by means of it. The so-called law of thermo-neutrality, of Hess, which has been confirmed, in part at least, by the well-known investigations of Thomsen and of Berthelot, is in complete accord with the theory of ionisation, and so are the exceptions to this law which must necessarily exist in cases of incomplete dissociation; whereas, without this theory the facts concerned constitute an incomprehensible puzzle.

It is similar with the identity of the heat of neutralisation of one and the same acid by means of different bases, and *vice versa*; also with the law of Oudemans and Landolt (in accordance with which the salts of optically active alkaloids and of optically active acids exhibit the same rotation in solutions of equivalent concentration), with the magnetic rotatory power, and with the atomic magnetism. Further, the principle in accordance with which the spectra of dilute solutions of different salts with similarly coloured ions are identical, and that according to which the molecular refractive power of the salts present in aqueous solution is an additive property, are explained in the same way. But probably the most important fact of this kind is that of the proportionality that exists between electrolytic conductivity and avidity in the case of acids, with which may be coupled the proof, furnished by Arrhenius, that the extent of the dissociation calculated from the electrolytic conductivity leads to very nearly the same results as that calculated from the depression of the freezing point. In these circumstances we cannot be in doubt as to whether the hypothesis of Arrhenius is warranted.

This ionisation theory, as it is now commonly called, leads us directly to electro-chemistry, which has undergone an advancement undreamt of twenty years ago, and has now developed into a separate branch of science that constantly leads to new scientific and practical results. The enthusiasm with which the discovery of the galvanic current and of the voltaic pile was welcomed, as sketched in Lecture V., was, as we now know, perfectly justified. And even although disillusionment followed the great discoveries of Ritter, Davy, Berzelius, and Faraday, and although this branch remained unfruitful for decades, still the opinion has been verified of those who believed that untold treasures lay here which should one day be disclosed.

The modern subject of electro-chemistry forms a continuation to those older discoveries, and to the important investigations of Hittorf and of Kohlrausch, which were now for the first time fully understood; and it leads to successive new discoveries.

In this connection, accumulators may first of all be mentioned here, since they have come into very general use, and without them it would scarcely be possible to employ electricity to advantage. Their introduction is the outcome of the discovery of polarisation by Ritter, and of the very exhaustive researches of Planté, which extend as far back as the year 1859. Planté constructed very powerful examples of the so-called secondary batteries; and these were afterwards improved upon in important particulars by Faure.

The devising by Lippmann of the capillary electrometer, which depends upon the change in the surface tension of mercury produced by polarisation, is also worthy of mention.

The theory of the voltaic pile, for which we are indebted to Nernst, is very important. It is founded upon the theory of diffusion, which was advanced by Nernst himself, and upon the idea of solution tension deduced from van 't Hoff's theory of solution. Nernst also developed the theory of concentration cells in the same way, and in doing so arrived at the same conclusions that Helmholtz had already reached by thermodynamical investigation.

These matters must, however, be disposed of here by merely alluding to them, since they really belong more to the domain of physics than to that of chemistry.

(To be continued).

ACTION OF ACETYL AND BENZOYL CHLORIDES ON DRIED COPPER SULPHATE ($CuSO_4.H_2O$).*

By W. R. HODGKINSON and Captain LEAHY, R.A.

THESE experiments were undertaken to ascertain whether there would be any ground for considering copper sulphate monohydrate as an acid body; the ratio of magnesium dissolved to copper deposited from a solution of copper sulphate (Clowes) suggesting such a nature.

Pure copper sulphate in fine powder was dried for a week at 98° C. An analysis showed that it contained exactly one molecule water. Weighed quantities of this salt were submitted to the action of acetyl chloride; firstly, by dissolving the chloride in metaxylene and agitating this with the fine powder of the copper salt and heating up to about 100° C. As this method was found to produce acetmetaxylene, $CH_3CO.C_6H_3(CH_3)_2$, it was abandoned.

Weighed quantities of the salt were then exposed in shallow platinum trays to the vapour of the chloride. After trying at several temperatures with varying results, it was found that an evident definite reaction took place when the vapour of the chloride was simply carried over the copper salt by a stream of well dried CO_2 at the ordinary temperature, 12—16° C. Under these circumstances the copper sulphate changed colour—from almost white to deep chocolate brown (copper sulphate monacetate)—and hydrogen chloride was evolved.

On heating the tube containing the tray with the salt to about 110° C., the compound evidently decomposed; it became quite white, acetic anhydride was given off, and the residue in the tray was pure $CuSO_4$. There was distinct evidence that at about 60—70° an intermediate compound was formed from the action of the excess of the chloride on the acetate first formed. This appeared to be a compound of the anhydride with the $CuSO_4$. Scarcely a trace of chlorine was retained by the copper salt.

Benzoylic chloride appeared to behave in a perfectly similar manner.

The figures obtained are not very close to theory, but scarcely leave any doubt about the composition of the products. In one experiment the copper salt absorbed 20·16 of acetyl. If the reaction proceeded according to $CuSO_4H_2O + CH_3COCl = HCl + CuSO_4CH_3COOH$, the gain in weight would be 23·72 per cent. In another

* Read before the British Association (Section B), Dover Meeting, 1899.

experiment, 48·28 per cent acetic anhydride was combined. On the assumption that the reaction—

$$CuSO_4CH_3COOH + CH_3COCl = HCl + CuSO_4CH_3COOOCH_3$$

took place, the gain in weight should be 47·45 per cent.

Similar results were obtained with benzoylic chloride.

Ordnance College, Woolwich.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 12th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during September was 2·38 inches, the thirty years average is 2·43 inches, making a deficiency of 0·05 inch; the total deficiency for the year is now 3·68 inches, or 19·9 per cent.

Our bacteriological examinations of 382 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, standpipes, &c., making a total of 421 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	170
New River, filtered (mean of 76 samples) ..	4
Thames, unfiltered (mean of 26 samples) ..	574
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 205 samples)	16
Ditto ditto .. .. highest	187
Ditto ditto .. .. lowest	1
River Lea, unfiltered (mean of 25 samples) ..	220
River Lea, from the East London Company's clear water well (mean of 25 samples) . ..	9

The waters of the Thames, Lea, and New River during September have been specially characterised by their extraordinary bacterial purity in the unfiltered state. Whereas in August the average microbic impurity of the Thames per c.c. was 2269, this month it is reduced to 574. The River Lea last month contained an average of 863 microbes, while this month it has been reduced to 220. The New River last month contained 410, and this month it has sunk to 170.

The raw water being so much better, the filtered water is of higher quality than usual. The purification by storage and regulated filtration has become so effective that, as we have pointed out again and again, the quality of the distributed water now is practically independent of variations in the microbic impurities that occur during the course of the year in the respective sources of supply.

When storage and filtration are effectively conducted, water is produced for distribution containing an average of less than 100 microbes per c.c. Such a result is regarded by the highest authorities as eminently satisfactory, and such a water has never been known to cause a water-borne disease. It will be noted in many of our reports and on many occasions that the clear-water wells of the London Companies contain far less than 100 microbes per c.c. It is true that some individual filter may become temporarily defective, such as, for instance, in the case of the Thames-derived sample this month, which gave 187 microbes per c.c.; but this is immediately detected and remedied within a short period of time, so that next day the microbial impurity of the water is almost invariably reduced below the recognised standard of 100. Owing to the large number of samples bacteriologically examined every month (amounting in September to 421), it is easy to ascertain and remedy at once any defective filter.

Taken as a whole, the quality of the London water supply has rarely, if ever, been so good as during the course of last month, and for any person, professing to be conversant with the question of water supply, to talk at the present day of the drinking water of London as a "limited supply of diluted sewage, in the place of fresh water," is to indulge in a misrepresentation of facts which cannot be too strongly condemned.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

LIQUID AIR AS AN ANALYTIC AGENT.*

By Professor DEWAR, M.A., LL.D., F.R.S.

(Concluded from p. 190).

Thermal Transparency at Low Temperatures.

PICTET, after an elaborate investigation, concluded that below a certain temperature all substances had practically the same thermal transparency, and that a non-conducting body became ineffective at low temperatures in shielding a vessel from the inflnx of heat. Experiments, about to be detailed, however, prove that such is not the case, the transference of heat observed by Pictet appearing to be due not so much to the materials themselves as to the air contained in their interstices. Good exhaustion in the ordinary vacuum vessels used in low temperature work reduces the influx of heat to one-fifth of what is conveyed when the annular space of such double-walled vessels is filled with air. If the interior walls are silvered, or excess of mercury is allowed to remain, the influx of heat is diminished to one-sixth of the amount entering without the metallic coating. The total effect due to the high vacuum and silvering is to reduce the ingoing heat to one-thirtieth of the original amount, *i.e.*, roughly, to 3½ per cent.

By filling the annular space between the walls of several similar vacuum vessels with various substances, and exhausting them all to the same low pressure, large differences in the thermal isolation were observed. The rate of evaporation of equal volumes of liquid air contained in the respective vessels measures the rate of influx of heat. Moreover, it appears that what might be called under the circumstances the thermal transparency of some materials diminished at very low temperatures instead of increasing, as had been asserted. Thus, of two

* A Lecture delivered before the Royal Institution of Great Britain, April 1, 1898.

vacuum tubes (one simply exhausted, and the other having powdered carbon in the vacuum space), the latter, at low temperature, was the most efficient preserver of liquid air, showing that the carbon diminished the radiation and gas convection. But when the vacuum was destroyed and air admitted into the space, the liquid air in the carbon tube boiled off much more vigorously than that in the simple tube, indicating that at ordinary temperatures carbon allowed more heat to pass than did air.

In conducting these experiments, generally sets of three double-walled glass tubes, as nearly identical in size and shape as possible, were mounted on a common stem, and two out of the three filled with different kinds of powders, while the third is left empty as a standard for comparison (Fig. 3). In this way each set had the same vacuum, and, as intercommunication between the tubes after sealing off from the pump was left free, any deterioration in the vacuum on keeping affected all three vacuum tubes to the same extent.

The preparation of such tubes entails enormous labour, because it takes days of exhaustion with a mercurial pump to extract the occluded gases, even at as high a temperature as the glass would stand. Before beginning the experiment, the vacuum tubes of each triple set were filled with liquid air, and allowed to stand half an hour in order to get the heat conduction in the porous mass into a steady state. The tubes after this treatment were filled to the same height, and the relative times required to distil off the same volume of liquid air from each observed, the outer surface of the vacuum tubes being maintained at a steady temperature by immersion in a large vessel of water. Neither the tubes nor the shape of the vacuum space in each were absolutely identical, so that the results are simply comparative. The general ratio of heat propagation found for two substances when different sets of double-walled tubes of about the same form and proportion were compared, remained substantially constant when a high vacuum was reached. A confirmation of the results was generally made by noting the time required to evaporate the whole of the air from each tube. The annular vacuum space had generally a thickness of 4 to 5 m.m., and was in each case completely filled up with the solid. In reality, however, the absolute fraction of the space filled by the solid did not exceed one-half. The effect of any considerable inequality in the thickness of the non-conducting powders was ascertained by comparing two vacuum tubes, one having double the thickness of vacuum space of the other, and each then filled with precipitated silica. Taking the unfilled vacuum tube as the unit for comparison described above, then the single thickness of silica increased the insulation to 6 and the the double thickness to 8. The following table contains the results of a number of experiments with triple sets of double-walled tubes filled with different substances, when exhausted and unexhausted. The results are expressed in the relative times required to volatilise the same small volume of liquid air from each tube. This is most readily done, after filling each tube with the same volume of

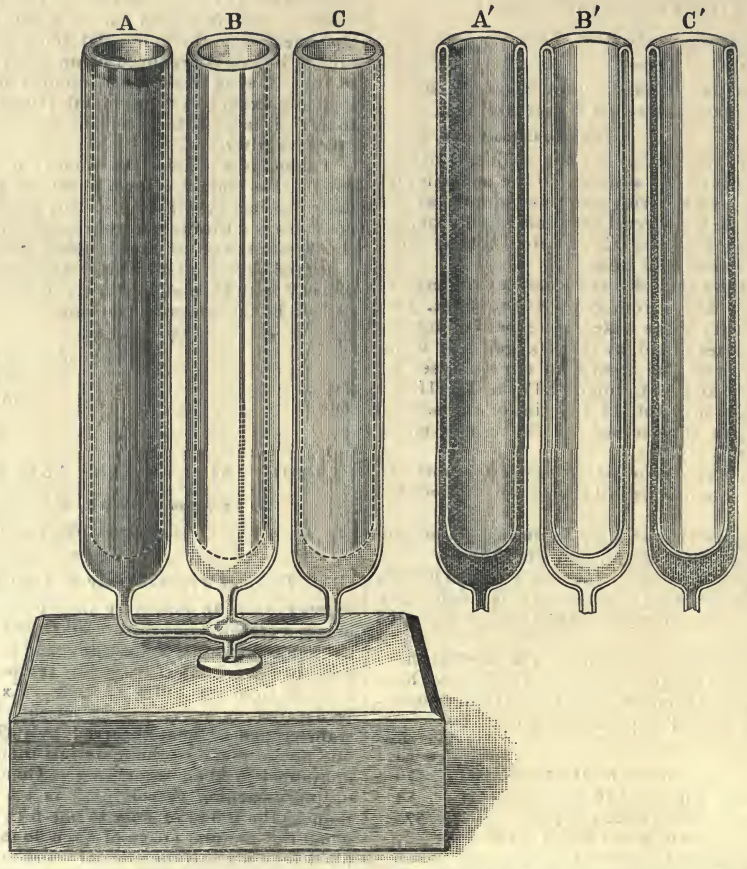

Fig. 3.—Three Tubes blown on to one Stem, so that the Exhaustion in each would be identical.

A, Filled with lampblack between the inner and outer tubes. B, Annular space left empty. C, Filled with silica between the tubes. A′, B′, C′, The same tubes in section.

liquid air by noting the time required to fill a given vessel standing over the pneumatic trough with the gaseous air distilling off.

In each triple set the unit taken for comparison is the time value of the free vacuum spaced tube.

	Vacuum.	Atmospheric pressure.
Empty tube	1	1·0
Charcoal	5	0·7
Magnesia	2	0·6

	Vacuum.	Air.
Empty tube	1	1·0
Lamp-black	5	0·7
Silica	4	0·7

	Vacuum.
Empty tube	1
Phosphorus (amorphous)	1
Mercuric iodide	1·5

Empty tube	1
Lead oxide	2
Bismuth oxide	6

From these experiments it will be seen that silica charcoal, lamp-black, and oxide of bismuth, all increase the insulation to 4, 5, and 6 times that of the empty vacuum space. In tubes generally which did not reach such a high vacuum the relative insulating effect of these powders could be raised as much as 1 to 8 or 1 to 10. In this case the influx of heat per unit of time in the vacuum tube which did not contain any finely divided powder was necessarily much greater. As the chief communication of heat is by molecular bombardment, the fine powders must shorten the free path of the gaseous molecules, and the slow conduction of heat through the porous mass must make the conveyance of heat energy more difficult than when the gas molecules could directly impinge upon the outer glass surface maintained at a higher temperature. To separate the true conduction from the radiation and the gas motion would require far more elaborate experiments, but these are sufficient to prove that the presence of certain finely divided solids in the high vacuum space of the vessels used in low temperature research improves the heat insulation, while in the presence of air the same bodies facilitate the transference of heat. This is the explanation of Pictet's apparently extraordinary results.

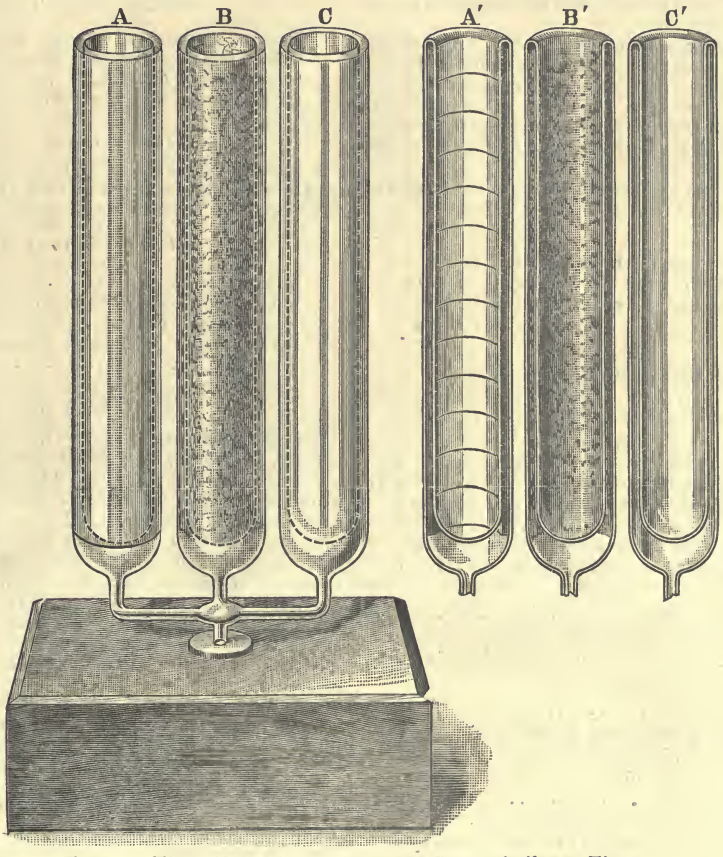

FIG. 4.—Three Tubes blown on to one Stem, similar to Fig. 3.

A, Vacuum space having three turns of gold paper, gold outside. B, Vacuum space having some pieces of gold leaf put in so as to make contact between walls of vacuum tube. C, Vacuum space empty. A′, B′, C′, The same tubes in section.

	Vacuum.
Empty tube	1
Graphite	1·3
Alumina	3·3

Empty tube	1
Lamp-black	4
Lycopodium	2·5

Empty tube	1
Calcium carbonate	2·5
„ fluoride	1·25

Empty tube	1
Barium carbonate	1·3
Calcium phosphate	2·7

In no case was the diminution of the influx of heat, in the case of the use of finely divided solids, ever so effective as a high vacuum, in an empty tube, the glass surfaces being silvered. This is seen by reference to results recorded in Tables Nos. 1, 2, and 3, where the insulation is increased in the proportion of more than 1 to 7, which is decidedly better than anything reached by the use of powders.

It will be noted that the use of silica and charcoal to fill up the annular spaces between the walls of these silver-coated vacuum vessels has produced very different results from those recorded in the former experiments with plane glass surfaces. Instead of the heat insulation being increased from 4 to 5 times by the use of such powders, it is now only very slightly benefited. This suggests that the finely divided solid affects chiefly the combined radiation and conduction factors.

A further set of experiments was made with similar vscuum tubes, replacing the powders by metallic and other septa (Fig. 4). Various papers coated with metallic powders in imitation of gold and silver which are in common use, were compared with black paper and a comparison made between the use of sheet lead and aluminium, all under similar conditions.

The following tables express the comparative results of the different experiments:—

(1).

Vacuum space empty, not silvered	1
Same space unexhausted	0·25
Vacuum space empty, silvered on both surfaces	7·4

(2).

Vacuum space empty, silvered on inside surfaces	1
Silica in silvered vacuum space	1·1

(3).

Empty silvered vacuum	1
Charcoal in silvered vacuum	1·25
Vacuum space unsilvered	1
,, silvered inside	5
,, in annular space with glass test-tube silvered	6

(4).

Vacuum space empty	1
Three turns silver paper, bright surface inside	4
Three turns silver paper, bright surface outside	4

(5).

Vacuum space empty	1
Three turns black paper, black outside	3
Three turns black paper, black inside	3

(6).

Vacuum space empty	1
Three turns gold paper, gold outside	4
Some pieces of gold leaf, put in so as to make contact between walls of vacuum tube ..	0·3

(7).

Vacuum space empty	1
Three turns, not touching, of sheet lead ..	4
Three turns, not touching, of sheet aluminium	4

The experiments show that liquid air can be conveniently used to study many important problems of heat transmission.

(To be continued).

On Hæmatine from Blood, and its Variations according to the Animal Species.—P. Cazeneuve and P. Breteau.—The authors give the results of their analyses of hæmatine from bullock, horse, and sheep's blood; they include the C, H, N, Fe, and O. They found the proportion of N to Fe to be 4·1 : 1 with bullock, 4·3 : 1 with horse, and 3·5 : 1 with sheep.—*Bull. Soc. Chim.*, xxi., No. 8.

VARIATIONS IN SEA-WATER, WITH THE DEPTH, PARTICULARLY WITH REGARD TO THEIR IODISED COMPOUNDS.

By A. GAUTIER.

WATER taken from the surface of the Atlantic does not contain a trace of iodides or iodates (*Bull. Soc. Chim.*, Series 3, xxi., 566). The whole of the iodine is found in the form of matter of a very complex nature,* and this element does not become apparent until after fusing the residue from the water with potash. In water taken at the entrance to the Channel, at 40 kilometres from the shore, I found:—

Iodine per Litre of Water.

	M.grms.
Mineral iodine	0·000
Iodine removed by the porcelain filter (organisms, &c.)	0·520
Latent iodine of the soluble compounds	1·820
Total per litre	2·320

I have just made similar observations with Mediterranean waters taken at the surface, 11 kilometres from the shore opposite Monaco, and I found:—

Iodlne per Litre of Water.

	M.grms.
Mineral iodine	0·000
Iodine removed by the porcelain filter (organisms, &c,)	0·286
Iodine from the soluble complex compounds	1·960
Total per litre	2·241

These results prove that:—1. Sea-water taken at the surface, in two seas far apart from each other, contain almost the same total iodine, it being understood that the samples are taken far from the mouths of rivers and after continued fine weather. 2. In the waters of the Mediterranean, as well as in that of the ocean, there is no trace of iodides or iodates to be found if the samples are taken at or within a few metres of the surface. 3. In sea-water the iodine is contained at the surface, partly in the insoluble and organised state and partly in the soluble state; in this case it forms part of complex compounds partially or totally organic, nitrated, phosphorised, and dialysable.

The nature of these soluble iodised compounds merits a much closer study, but it is not without difficulties; the iodised matter disappears from the sea-water when it is concentrated. Water which I collected in salt-marshes evaporated spontaneously in the air, and, showing 24° B., did not contain the least trace of mineral or organic iodine. A small quantity of phosphates still remain, but the lime was entirely precipitated, probably carrying with it the iodised material.

Whatever may be the nature of this complex iodised substance, my opinion is that, coming from the depths of the sea, and contained originally in the primitive rocks, then in the water in the mineral form, the iodine, when it arrives in those regions of the sea rich in living organisms capable of assimilating it, passes partially or totally into the organic state. This phenomenon, which thus causes the disappearance of the mineral iodine, should be at its maximum in that portion of the sea which is penetrated by light, and should diminish—without, perhaps, entirely disappearing—in the lower regions of the sea which are plunged in absolute darkness. If things do happen in this manner, we may hope to find, at depths of from 400 to 500 metres, and lower, where algæ no longer exist

* These compounds are entirely or partly organic, but I have not yet decided the point as to whether calcareous iodosulphates or iodophosphates, mixed or feebly united, are found.

and only a few rare living organisms are found, iodine in its primitive form—that is to say, mineral.

To submit this theory to the test of experiment, I first had recourse to the waters of the Mediterranean, the temperature of which is almost invariable (about 13°), and where it has been found that below a depth of 300 metres there is complete repose, so that the different layers of water are not mixed by any currents. For the purpose of collecting samples I am indebted to the great kindness of His Highness the Prince of Monaco, whose zeal for everything connected with oceanography is well known. By his help I was enabled to take samples of water at different depths. These were taken on the 10th of May last, after continued fine weather, at 11 kilometres from the shore opposite Monaco. Four samples of 2 litres each were taken in the same vertical line,—the first at 0·5 metre below the surface, the second at 780 metres, the third at 880 metres, and the last at 980 metres in depth, where the bottom, formed of a reddish sandy clay, was touched. For the purpose of noticing, first of all, the influence which the living organisms inhabiting it might have on the water, and particularly on its iodised compounds, it was necessary to measure their mass, and even to determine the nature of those which might also be found below the region near the surface. For this purpose the 2 litres of water taken at 780 metres were immediately treated with 1/50th of formol, a substance which immediately fixes the plasmas and living matters in the state in which they are found, and which thus allows them to be collected and examined under the microscope for the purpose of observing the state in which they exist at the moment of this species of embalming. The waters from 780 metres thus formolised were allowed to stand for twelve days to deposit all matters in suspension, and then carefully syphoned off, and the bottom layer with the deposit was run into a glass tube 1 metre long, drawn out and closed at the end. This was left for ten days longer; the deposit was then collected at the bottom by centrifugal force without having undergone any filtration. In 2 litres only 1/15th of a m.grm. was found; this was examined under the microscope, but did not contain any living algæ; it consisted principally of mineral (quartz) splinters or flakes, yellow and brown scales with an articulated appearance, formless masses having the appearance of protoplasm become granular, oily, and discoloured, and a few sponge spiculæ; there were also found three or four siliceous envelopes of diatoms, a foraminifera shell, a few bacteria; finally a small copepod, living at the moment of capture, and, according to its volume, weighing about 0·15 m.grm. In a word, at a depth of 780 metres, with the exception of this little crustacean, no other living organisms were found besides a few very rare protozoa and bacteria, representing a proportion of 1/10th at the most of the accompanying *débris*, and which themselves had a total weight of not more than 1/30th of a m.grm. per litre of water.

The total absence of microscopic algæ and the very small mass of the other living organisms thus established at this level, and *a fortiori* at lower levels, it became interesting to find what influence the disappearance of these organisms had on the composition of sea-water, especially with regard to the variation of the iodised compounds. We therefore examined comparatively the samples taken at the surface, at 880 metres, and at 980 metres; these samples were taken in ground-glass stoppered bottles, and kept in the dark until they were analysed. These waters were examined for their density; their total solids; their total chlorine, bromine, and iodine; their richness in iodine, and the nature of their iodine compounds.

Density at Different Depths.—This was taken at 4° and on 250 c.c. at a time, for greater accuracy; we found:—

	Density.	Weight of 1 litre at 4°.
Surface..	1·03014	1030·14 grms.
880 metres	1·03104	1031·04 ,,
980 ,, ...	1·03076	1030·76 ,,

The density of the water at the bottom is, as we see, slightly less than that of the water taken 100 metres higher up. The small difference is only 0·28 grm. less in a litre; this is confirmed, as will be seen, by the weight of the dry residue, as well as by other estimations. It is probable that the sea receives, especially at points near high moutains, as is here the case, fresh water from deep springs, which slightly diminish the density of the water at the bottom, and which only mixes very slowly by diffusion with the sea-water, which is here quite at rest.

Dry Residue.—This was taken on 10 c.c. of water measured at 4°; to it was added 0·02 of dry carbonate of soda, to prevent loss by dissociation on heating; we then deduct the weight of the salt added: complete desiccation was effected at 105° until the weight was constant; we found:—

	Dry resiuue per litre at 4°.
Surface	43·40 m.grms.
880 metres	44·78 ,,
980 ,, ...	43·41 ,,

These weights are very high: the weight of salts per litre is from 35 to 38 grms. in the Atlantic; Laurent found 40·7 grms. per litre in the Mediterranean, near Marseilles; but our three weights agree among themselves.

Chlorine—Bromine—Iodine.—The total weight of these three elements was:—

	Chlorobromoiodide of Ag per litre at 4°.	Corresponding theoretical amount of NaCl.
Surface ..	0·8579 m.grm.	34·92 m.grms.
880 metres	0·8844 ,,	35·99 ,,
980 ,,	0·8767 ,,	35·68 ,,

The sea-salt thus calculated is certainly too high, the alkaline-earthy chlorides being here transformed by the calculation into chloride of sodium. But we still notice that the principal salts are more abundant at a depth of 880 metres than at 100 metres lower down.

Iodised Compounds.—The water examined from this point of view, three days after the sample was taken, had not been exposed to light for an instant; it was necessary, in fact, to prevent the modifications which the living organisms might undergo under its influence, particularly with regard to the iodised compounds. The matter in suspension, living or not, was separated by filtration through porcelain in the dark. The iodine was then estimated in its three forms, as has been already described in a previous paper. We found:—

Iodine per Litre (*Surface*).

	M.grms.
Iodine removed by the filter (living organisms, insoluble bodies, &c.)	0·286
Iodine entirely or partially organic, in the soluble state	1·960
Mineral iodine (iodides, iodates, &c.) ..	0·000
Total	2·246

Iodine per Litre (880 *Metres*).

Iodine removed by the filter (organic matter, &c.)	0·100
Iodine entirely or partially organic, in the soluble state	2·130
Mineral iodine (iodides, &c.)	0·150
Total	2·380

Iodine per Litre (980 *Metres*).

Iodine removed by the filter (organic matter, &c.)	0·065
Iodine entirely or partially organic, in the soluble state	1·890
Mineral iodine (iodides, &c.)	0·305
Total	2·260

The examination of these figures leads to the following conclutions:—1. The total iodine of the waters of the Mediterranean is practically constant from the surface to the bottom of the sea; the intermediate layer at 880 metres always contains a slightly greater proportion. 2. The water of the Mediterranean appears, on the surface, to contain slightly less total iodine (2·25 m.grms.) than that of the open sea (2·40 m.grms.) per litre. 3. As the living organisms, algæ or protozoa, increase in the water, the mineral iodine as iodides and iodates diminishes —from 0·305 m.grm. per litre at the bottom, it becomes 0·150 m.grm. at 100 metres above, and it has totally disappeared at the surface, and probably long before that point. This result confirms the preconceived ideas which have guided us in this research. 4. On the contrary, as the organic iodine diminishes the organised iodine increases as we leave the bottom, and at the same time as the mass of living organisms which fixes this element increases. 5. The totally or partially organised iodine—that is, the iodine in the soluble state forming part of the matter which goes through the filter—does not sensibly vary, although in the case of the Mediterranean it appears to have a slight maximum at about 880 metres. The substance from which this iodine is derived does not seem necessarily to belong to the living organisms—so numerous at the surface, and so rare, as we have seen, from 400 metres downwards.

It is altogether remarkable to observe the existence at all levels in the Mediterranean, as in the open sea, of this totally or partially soluble organic matter, as well as of the glutinous material retained by the filter. These two substances, both very rich in iodine and very complex, were found in every case, although they are a little less abundant at the greatest depths; they merit a special study to themselves.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 16.

COMPARATIVE ACCURACY OF TITRIMETRIC AND GASOMETIC METHODS OF ESTIMATING HYDROGEN DIOXIDE IN PRESENCE OF VARIOUS PRESERVATIVE AGENTS.*

By CARL E. SMITH.

(Concluded from p. 195).

Titrimetric Thiosulphate Method.—This was first recommended by C. T. Kingzett (*Journ. Chem. Soc.*, 1880, vol. xxxvii., p. 802), and later by H. Thoms (*Arch. Pharm.*, 1887, vol. xxxv., pp. 335—343). It is based on the fact that hydrogen dioxide liberates a definite quantity of iodine from iodides in acid solution, the iodine being titrated with sodium thiosulphate in the usual manner.

$$H_2O_2 + 2KI + H_2SO_4 = I_2K_2 + SO_4 + 2H_2O;$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

Thoms proceeds by warming 0·5 grm. of potassium iodide, 1 grm. of 20 per cent sulphuric acid, and 50 c.c. of water to 40° C., adding 0·5 c.c. of the hydrogen dioxide solution, shaking about five minutes, and titrating the liberated iodine with N/10 thiosulphate, then warming again to 40°, again titrating the appearing iodine, and repeating until no further liberation of iodine takes place. Carried out in this way the method is rather slow and tedious, requiring at least fifteen minutes for completion; but, since it was stated to be accurate, the writer decided to include it in his experiments, and found later, that by omitting the greater part of the water, so as to reduce the bulk of the solution to about 15 c.c. for the above-mentioned quantities, heating might be dispensed with, and the reaction would nevertheless be ended within five minutes. The final result was found to be the same, whether working with dilute or with concentrated solutions. One possible source of error with the latter is that, when standing in a very warm room prior to titration, slight losses of iodine might occur through vaporisation. This could, of course, be readily seen and proper precautions taken to prevent loss. The following mode of operation is considered the most practical:—Dilute the solution to be tested to exactly ten times its volume with distilled water, measure 5·6 c.c. of the dilution (=0·56 c.c. of sample) into a beaker or flask, add 5 c.c. of 10 per cent sulphuric acid and 5 c.c. of a 10 per cent solution of potassium iodide, and let the mixture stand for five minutes. Then gradually add N/10 thiosulphate, with constant agitation, until the colour of the solution is discharged. If the solution remains colourless upon standing a few minutes longer, the titration is finished. If a colour should appear, add sufficient thiosulphate solution to remove it. The total number of cubic centimetres of the thiosulphate solution required indicates the number of volumes of available oxygen the sample contains. If it is considerably stronger than ten volumes, the result will probably be too low, unless more time is allowed for the reaction. In such a case correspondingly more potassium iodide and sulphuric acid should be taken. No starch paste is necessary, as the end-reaction is sufficiently sharp without it, particularly when the solution is placed over a white surface. In cases in which an accurate dilution of the sample is impracticable, 1 c.c. of the undiluted sample may be taken, with double the quantities of reagents given above. The number of cubic centimetres of N/10 thiosulphate required must then be multiplied by 0·56 to obtain the strength in available oxygen. Or, instead of N/10 thiosulphate (24·8 grms. of crystallised salt per litre), a solution containing 44·29 grms. per litre may be used. In the latter case each cubic centimetre consumed indicates one volume of available oxygen, provided 1 c.c. of sample has been taken. The per cent of hydrogen dioxide is obtained by multiplying the volume strength by 0·3038. (This is not strictly correct, as the specific gravity of the solution is left out of consideration). It is important that the reagents used are free from such impurities as would act as reducing or oxidising agents. The sulphuric acid should be free from sulphurous, arsenious, and nitric acids, and the potassium iodide from iodate. Sodium thiosulphate (commercially called "hyposulphite of soda") is very frequently found in the market of a sufficiently high degree of purity to make it permissible to prepare the N/10 solution for the assay of hydrogen dioxide, by dissolving exactly 24·8 grms. of it in enough distilled water to make 1 litre, instead of standardising it with iodine. It should be in colourless, transparent, uneffloresced crystals, and contain no chloride or sulphate, or at most only traces of sulphate. The crystals should be coarsely powdered, and any interstitial mother-liquor removed by pressing between folds of bibulous paper before weighing. The writer, however, prefers to re-crystallise the commercial salt, and finds the solution prepared from this, in the manner indicated above, fully as accurate as when standardised with pure iodine.

This method has been treated of more at length than the others, because it proved to be the best of those examined, as will be explained more fully below.

Comparison of Methods on Commercial Samples.—A few commercial solutions of hydrogen dioxide of varying strength and purity were examined with the object of gaining some knowledge of the comparative accuracy of the four methods described. The pharmacopœial tests were also applied, and the results embodied in Table I.

No barium salts or fluorides were detected by the U.S.P. tests. The limit of acid (0·5 c.c. of N/1 soda for 50 c.c.) was exceeded in three samples. The limit of residue (0·25 grm. for 50 c.c.) was exceeded in one. Nos. I., II., and III. are aqueous solutions, stated to contain respectively 10, 15, and 30 volumes of available oxygen,

* Report from Research Committee D, Section II., of the Committee of Revision of the U.S. Pharmacopœia. From the *American Journal of Pharmacy*.

TABLE I.

	Sample I.	Sample II.	Sample III.	Sample IV.
Strength by $KMnO_4$ (titrimetric) method..	10·3, 10·35 vol.	15·45, 15·45 vol.	29·45, 29·35 vol.	26·65, 26·65 p.c.
Strength by $KMnO_4$ (gasometric) method..	10·6, 10·3, 10·1, 10·4 vol.	15·5, 15·35 vol.	30·15, 31·6 vol.	27·85, 26·75 p.c.
Strength by $Ca(ClO)_2$ method	10·45, 10·4 vol.	15·5, 15·55 vol.	29·7, 29·9 vol.	26·95, 27·2, 27·1 p.c.
Strength by $Na_2S_2O_3$ method	10·3, 10·35 vol.	15·5, 15·55 vol.	29·4, 29·4 vol.	26·2, 26·4 p.c.
Acidity in c.c. of N/1 soda required for 50 c.c.	1·85 c.c.	0·95 c.c.	2·1 c.c.	Neutral
Residue from 50 c.c. at 100° C.	0·339 grm.	0·029 grm.	0·124 grm.	0·015 grm. from one tube (3·025 grm.).
Impurities found	HCl, NaCl, H_3PO_4	HCl, H_3PO_4	HCl, H_2SO_4, H_3PO_4	Not identified

TABLE II.

Substances added.	Permanganate method (titrimetric).	Hypochlorite method.	Thiosulphate method.
Glycerin, 5 per cent	10·55, 10·45	10·2, 10·25	10·25, 10·25
Boroglycerin, 5 per cent ..	10·45, 10·5	10·15, 10·05	10·25, 10·3
Boric acid, 5 per cent.. ..	10·3, 10·25	10·3, 10·2	10·3, 10·25
Boric acid, 20 per cent ..	10·3, 10·3	10·1, 10·15	10·3, 10·35
Salicylic acid, 0·2 per cent..	11·3, 11·5	9·6, 9·7	10·3, 10·3
Salicylic acid, 2 per cent ..	15·0	9·55, 9·4	10·3, 10·4
Benzoic acid, 0·2 per cent..	10·45, 10·4	10·15, 10·15	10·45, 10·4
Salol, saturated solution* ..	10·25, 10·25	10·0, 9·85	10·2, 10·2
Acetanilide, 0·5 per cent ..	10·3, 10·3	10·1, 10·2	10·25, 10·25
Ether, 10 per cent	10·35, 10·35	10·65, 10·7	10·25, 10·25

* Prepared by diluting 13·35 c.c. of H_2O_2 solution with a cold, aqueous, saturated solution of salol to 100 c.c.

TABLE III.

Grms. of glycerin added to 1 c.c. of solution.	Permanganate method (titrimetric).	Permanganate method (gasometric).	Hypochlorite method.	Thiosulphate method.
0·5	10·8			
1	11·25, 11·2	9·95, 9·8	10·5, 10·55	10·3, 10·3
2	12·25		10·5, 10·4	10·35

while No. IV. is an ethereal solution claimed to contain 25 per cent of hydrogen dioxide. These claims as to strength are reasonably well supported by the results obtained. It will be seen that with some samples the results by the different methods vary more than with others, the differences being greatest in the case of Sample IV. Subsequent experiments showed the discrepancies in this case to be at least partially due to the presence of ether, and the fourth method to be the most trustworthy for the assay of ethereal solutions. The first, third, and fourth methods are fairly well in accord with each other, but the second frequently gave figures differing not only from those obtained by other methods, but also differing widely among themselves in duplicate estimations. This method, because of its seeming unreliability, was left out of consideration in later experiments.

Estimation in presence of Preservative Agents.—In the experiments to be described, Sample II. was used, as it proved to be the purest of the aqueous solutions at the writer's disposal. The mixtures were prepared by diluting 13·35 c.c. of this solution, containing 15·45 volumes of available oxygen, to 100 c.c. with distilled water, after adding a definite quantity of the substance whose influence on the methods was to be determined. Five c.c. of the dilution represent 1 c.c. of a solution of two-thirds the above strength, or 10·3 volumes. It was thought best to base the calculations on this latter standard of strength, as being the more customary one. The percentages given in Table II., of preservative substances added, were also based on this standard. In some cases these were added in the quantity that would be required to make a saturated solution in the amount of 10 volume solution present; in other cases, much larger quantities were taken. The results are given in volumes of available oxygen.

These results show that the accuracy of the titrimetric permanganate method is affected slightly by the presence of moderate quantities of glycerin or boroglycerin, but that in the presence of the quantities that would be added to the solutions by manufacturers, which would hardly exceed 1 per cent, the difference in result would not be noticeable. In presence of salicylic acid, however, the method is worthless. There is evidence, also, that ether is not entirely without influence. It may be stated, then, as a generalisation, that in presence of organic substances, titration with potassium permanganate cannot be depended upon to always give sufficiently accurate results for pharmacopœial purposes.

With the hypochlorite method there is a tendency toward low results, most marked in presence of salicylic acid. The presence of ether introduces an error, which is probably due largely to the increased vapour tension. While the inaccuracies of some of the results of this method may be partially attributed to a neglect to make corrections for variation in barometric pressure and for the tension of water-vapour, it was proven by parallel estimations during the same atmospheric pressure, that some of the added substances without doubt exert an influence on the volume of gas liberated. This method, then, is also unreliable in presence of organic matter, but less so than the permanganate methods.

The accuracy of the thiosulphate method is practically unaffected by the addition of any of the substances given in Table II. The differences in the results are probably due as much to variation in measuring, &c., as to any other cause, and it would seem that, under such conditions as are at all likely to occur in practice, the method can be depended upon to give very serviceable results.

Estimation in presence of Larger Quantities of Glycerin.—In view of the fact that hydrogen dioxide is sometimes used medicinally in combination with glycerin, and that assays of such mixtures, containing comparatively large proportions of glycerin, may become necessary, trials were made to determine the comparative accuracy of the several methods under such conditions. A 10·3 volume solution was used, and the results are stated in volume strength (Table III.).

It is seen that the thiosulphate method is first and the hypochlorite second in point of accuracy, while the two

others are worthless. With permanganate the reaction is at first extremely slow, but it gradually quickens and the permanganate is decolorised as rapidly as it is added until near the end, when it again becomes very slow.

Summary.—The titrimetric permanganate method is accurate and reliable for the valuation of solutions containing only mineral acids and their alkali salts as impurities. With solutions containing glycerin or boroglycerin in quantities below 5 per cent the results are but slightly raised; in presence of larger amounts the method is inapplicable. Ethereal solutions give results a little too high. Salicylic acid interferes seriously, even in small quantity. The use of this method should be avoided whenever organic matters are suspected to be present. Applied gasometrically, the permanganate method is unreliable in all cases.

The hypochlorite method gives serviceable results in absence of preservatives. In their presence they are liable to fall too low, and with ethereal solutions they are too high.

The thiosulphate method is simple, rapid, and accurate, and its accuracy is not lessened by the presence of the usual preservative agents, nor by large quantities of glycerin. It is applicable in all cases, so far as known. It can be said of gasometric determinations in general, that they require more time, attention, and apparatus than titration methods, and that the results obtained by them cannot be expected to approach the latter in accuracy, unless suitable corrections, requiring tedious calculations, are made for variation in temperature and atmospheric pressure at least.

THE DEFINITION OF THE ELEMENT.*

By F. P. VENABLE.

It is with hesitation that I enter upon so speculative a discussion as the nature of the elements, and yet there are reasons why it should prove of great profit to draw the attention of this representative gathering of the chemists of America to this subject. We have nearly reached the close of the first century in which these elements have been the subject of experimental research. The ingenuity and the patient labour of an army of workers have been directed at the solution of the many problems connected with these elementary substances, and the ultimate aim, the goal, of all their striving has been the discovery of the properties and the nature of the atom.

It is eminently fitting that, as we stand at the threshold of the new century, we glance back along the road we have already come and take some account of the progress we have made. The quicksands of mere speculation must be avoided, and yet the mental vision, the "scientific imagination," must be called into service in considering that which so far transcends our cruder actual vision as the incomparable atom itself. There is another reason for considering the nature of the elements. At several times during the century a wider vision has made it necessary to recast the definition of the elements to accord with increasing knowledge. It would seem as if another such period of change were approaching. There may be need of a truer definition, and how shall this be realised or the new definition properly fitted unless the knowledge gained be summed up and appreciated?

The conception of an element among the Greek philosophers and the earlier alchemists was very different from the modern idea. This conception sprang from the theories as to the formation of the material universe. The elements were the primal forms of matter seen only combined, impure, imperfect. They were the essences or principles out of which all things were evolved. In the four-element theory, which was so widely spread among the ancients, the fire, air, earth, and water were not the ordinary substances known under these names, but the pure essences bestowing upon fire and water their peculiar properties. These essences were not thought of as actual substances capable of a separate material existence, and gradually the belief that a transmutation was possible between them sprang up. Thus they themselves might be derived from some one of them, as fire or water. The Thalesian theory, deriving all things from water, was especially popular, and was not completely overthrown until the modern era.

When, later on, the alchemist conceived of all metals as composed of sulphur and mercury, it was an essence or spirit of mercury that was meant. Certain common characteristics—as lustre, malleability, fusibility, combustibility, &c.—naturally led them to think of the metals as belonging to the same order of substances containing the same principles, the relative proportions and purity of which determined the variations in the observed properties. Thus the properties of the metals depended upon the purity of the mercury and sulphur in them, the quantities of them, and their degree of fixation. The more easily a metal was oxidised on being heated, the more sulphur it contained, and this sulphur also determined its changeability. The more malleable it was, the more mercury entered into its composition. If only something could be found which would remove the grossness from these essences, some unchanging, all-powerful essence, which, because of their search for it, gradually became known as the "philosopher's stone," then the baser metals might be transmuted into the noble gold when the sulphur and mercury were perfectly balanced and free from all distempers.

As has been said, these principles entering, all or some of them, into every known substance, were supposed to be not necessarily capable of individual existence themselves. This was the view held by the followers of Aristotle. With the reaction against the domination of the scholiasts, other views began to be held. It was Boyle who first gave voice to these changed views, in his "Sceptical Chemist" (1661). He defined elements as "certain primitive bodies, which, not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixed bodies are immediately compounded, and into which they are ultimately resolved." He, however, did not believe himself warranted, from the knowledge then possessed, in claiming the positive existence of such elements.

But little attention was paid to the subject by the subsequent chemists. The phlogistics were too much occupied with their theory of combustion, and none could see the bearing of this question and its importance to exact science.

Macquer, in his "Dictionary of Chemistry" (1777) words his definition as follows:—"Those bodies are called elements which are so simple that they cannot by any known means be decomposed or even altered, and which also enter as principles or constituent parts into the combination of other bodies." To this he adds:—"The bodies in which this simplicity has been observed are fire, air, and the purest earth." In all of this may be observed the resolution of observed forms of matter into primal principles, following the dream of Lucretius and the early Epicurean philosophers, a dream abandoned by the atomic school following, though largely holding to the same definition.

It was only when chemists began to realise that mere observation of properties, chiefly physical, was not sufficient, that the subject began to clear up and lose its vagueness. Black proved that certain substances were possessed of a constant and definite composition and fixed properties, unalterable, and hence simple bodies or elements. Lavoisier finally cleared the way for the work of the nineteenth century by his definition that "an element is a substance from which no simpler body has yet been

* Address of the Vice-President before Section C—Chemistry—of the American Association for the Advancement of Science, at the Columbus Meeting, August, 1899.

obtained; a body in which no change causes a diminution of weight. Every substance is to be regarded as an element until it is proved to be otherwise." With this clear definition to build upon, a rational system of chemistry became, for the first time, a posibility.

Thus the elements were recognised as simple bodies because there were no simpler. They were not complex or compound. The distinction was clearly drawn between bodies simple and bodies compound, and the name simple body has been frequently used as a synonym for element through a large part of this century. Naturally the question of simplicity was first settled by an appeal to that great arbiter of chemical questions, the balance. And, quite as naturally, many blunders were made, and the list of bodies erroneously supposed to be simple was very large. All whose weight could not be reduced were considered elementary. When, however, from such a body, something of lesser weight could be produced, its supposed simplicity was, of course, disproved.

This test for the elemental character has been clung to persistently, and is perhaps still taught, although it was long ago recognised that many of the elements existed in different forms, a phenomenon to which Berzelius gave the name *allotropism*. One only of these could be simplest, and the others could be reduced to this one and rendered specifically lighter. With the discovery of this relation it should have been quite apparent that the old definition would no longer hold good. But many years passed before chemists were made to feel that a new definition was necessary, and adapted one to the newer knowledge.

The insight into what Lucretius would call "the nature of things" was becoming clearer; the mental grasp upon these elusive atoms about which the old Epicurean reasoned so shrewdly was becoming firmer. Through what one must regard as the veil interposed by the earlier idea of the element, the chemist began to grope after the constituent particle or atom. It must be borne in mind that the definition of the element was largely formulated before the resuscitation of the atomic theory by Dalton, and the mental picture of the one has perhaps retarded the clearing up of the ideas concerning the other. From the atomic point of view the element was next defined as one in which the molecules or divisible parts were made up of similar indivisible particles. This afforded an easy explanation of allotropism as a change in the number of atoms in a molecule. As Remsen says: "An element is a substance made up of atoms of the same kind; a compound is a substance made up of elements of unlike kind."

Laying aside, then, all vaguely formulated ideas of essences, or principles, or simple bodies, or elemental forms, we found our present building upon the conception of the ultimate particle, be this molecule or atom.

As to this atom some clear conception is needed, and here we come to the *crux* of the modern theories. The chemist regards this atom as a particle of matter, and is unwilling to accept the theory of Boscovich that it is infinitely small, and hence a mathematical point, nor can he admit that it is merely a resisting point, and hence that all matter is but a system of forces. And yet it seems as though some authorities would lead up to such a conclusion.

While we need not consider these atoms as mere centres of forces, we are compelled to study them by the operation of forces upon them. What are called their properties have been studied and recorded with great care. These properties are evinced in the action of the forces upon matter, and the exhibition of force without matter cannot be admitted. This study of the properties has been the especial occupation of the century now closing, and so the elemental atom has come to be regarded as a collection of properties. As Pattison-Muir puts it ("Alchemical Essence and the Chemical Elements," p. 31):—"The name copper is used to distinguish a certain group of properties, that we always find associated together, from other groups of associated properties, and if we do not find the group of properties connoted by the term copper we do not find copper."

These properties are exhibited by the action of a small group of forces. Perhaps we do not know all of the forces; certain it is that we do not accurately know all of the properties, but, to quote Pattison-Muir again:—"The discovery of new properties always associated with a group of properties we call copper would not invalidate the statement that copper is always copper."

The properties of an atom are either primary, inherent and as unchanging as the atom itself, or they are secondary and dependent upon the influence of the other atoms, or varying with the change of conditions. To the first class belong such properties as the atomic weight, atomic heat, specific gravity, &c.; to the second, chemical affinity, valence, &c. In all the study of the atom the distinction between these should be carefully maintained in order that there may be clear thinking.

(To be continued).

OBITUARY.

GENERAL A. DE COURCY SCOTT, R.E.

We regret to record the death, on Monday last week, at his residence in South Kensington, of Major-General A. de Courcy Scott, R.E., the Official Water Examiner under the Metropolis Water Act, 1871. Deceased received this appointment early in 1887, on the death of Sir Francis Bolton, who had filled the position of Water Examiner from the date of the passing of the Act. When the vacancy occurred, it was thought that the post would be offered to Dr. (afterwards Sir Edward) Frankland, but in giving it to an ex-officer of Engineers the Local Government Board probably wished to ensure a continuity of the practice instituted by his predecessor. General Scott was conversant with the London Water Question, having published a pamphlet entitled "London Water: A Review of the Present Condition and Suggested Improvements of the Metropolitan Water Supply;" and, further, he was an examiner in the Science and Art Department at South Kensington. He was one of the members of the present Royal Commission; and it is a singular circumstance that he is the second of that body who has been removed by death before the result of their investigations is made known—Mr. H. W. Cripps having died a short time ago. Moreover, the Local Government Board have lost, by the death of Sir Edward Frankland and General Scott, the two officials on whom they relied for advice on water questions. It only remains to say that deceased entered the Royal Engineers in 1853 as a second lieutenant, and was present at the siege of Sebastopol; receiving the medal with clasp and also the Turkish medal. He retired in 1884 with the rank of Major-General.—*Journal of Gas Lighting*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 15, October 9, 1899.

Stereochemistry of Nitrogen.—J. A. Le Bel.—There seems to be no doubt that both optic and chemical isomerism exists in those derivatives of ammonium chloride, which include round the nitrogen atom four different radicles, and which contain six atoms of carbon at the least. Though the author's experiments, besides those of

Wedekind, have established the fact that bodies containing, at the least, six atoms of carbon have a stable geometric form, experiment has not yet been able to show whether this form is a pyramid with a square base or a double tetrahedron. The first hypothesis allows of three chemical isomers, the second of four, but at present only two are known; therefore all discussion on this subject is necessarily premature.

Reversible Liquefaction of Albumenoids. — M. Tsvett.— The author finds that various organic substances, such as the dioxybenzols (resorcine, pyrocatechin), phenol, chloral hydrate, &c., are susceptible of increasing the swelling up and the solution in water of many of the principal albumenoids. Under certain conditions of concentration the albumenoid matter passes, after swelling up, into the state of a true liquid. This solution in, and liquefaction of, albumenoids in aqueous resorcine is not connected with a chemical modification; the albumenoid will return to its original state by means of dialysis or precipitation by water. The phenomenon is, in fact, reversible.

Volumetric Estimation of Quinones derived from Benzene.—Amand Valeur.—The method of estimation which the author proposes is based on the reduction of the quinones by hydriodic acid. Instead, however, of using the free acid, an equivalent mixture of hydrochloric acid and potassium iodide is used. The results show that the action of this mixture on the quinones is instantaneous, and takes place according to the equation $C_6H_4O_2+2HCl+2KI=C_6H_6O_2+2KCl+I_2$. The iodine liberated remains dissolved in the undecomposed iodide of potassium. It can be titrated with great accuracy by means of sodium thiosulphate.

MEETINGS FOR THE WEEK.

THURSDAY, Nov. 2nd.—Chemical, 8. "The Theory of Saponification," by J. Lewkowitsch. "The Action of Dilute Nitric Acid on Oleic and Elaidic Acids," by F. G. Edmed. "Tetrazoline," by Siegfried Ruhemann and H. E. Stapleton. "On Ethylic Dibromobutanetetracarboxylate and the Synthesis of Tetrahydrofurfural-α-α'-dicarboxylic Acid," by Bevan Lean, D.Sc., B.A. "Camphoroxime,"—Part III. Behaviour of Camphoroxime towards Potassium Hypobromite," and "Optical Influence of an Unsaturated Linkage on certain Derivatives of Bornylamine," by M. O. Forster, Ph.D., D.Sc.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2084.

A NEW RADIO-ACTIVE MATERIAL.

By A. DEBIERNE.

M. AND MME. CURIE have shown that the radio-active property of pitchblende is not only due to the uranium contained in the mineral. Examination of the different substances which this mineral contains have led to the conclusion that there are present two new radiant elements, polonium and radium, both more active than uranium.

Polonium is an element closely akin to bismuth, accompanying the latter in all chemical reactions, but from which it can be slowly separated by repeated fractionations.

Radium resembles barium in its chemical reactions, and again it is only by repeated fractionations that a separation can be effected.

The individuality of these new elements, revealed only by their radio-activity, has been confirmed in one case by M. Demarçay. It appears therefore that this property of emitting radiation is sufficient to characterise chemical elements. I have examined other radiant parts of pitchblende. My researches have been chiefly carried out on that portion of the acid solution of pitchblende which is not precipitated by sulphuretted hydrogen, and is precipitated completely by ammonia or ammonium sulphide.

The material with which I started was almost free from uranium. The quantity of radiant products contained in it appeared to be very slight; so the first part of the research consisted in working up a great quantity of the substance, many hundreds of kilogrms., and eliminating as completely as possible the known radiant matter (polonium and radium).

The major portion of the product precipitated by ammonia is composed of iron and aluminium oxide, but besides these substances I recognised the presence of a considerable number of others which are present in very small quantities. I then separated the little quantity of zinc, manganese, chromium, vanadium, uranium, titanium, niobium, and tantalum. There were present also some of the rare earths of which I recognised lanthanum, didymium, cerium, and the yttria earths.

The radio-activity, which exists in a slight degree in the total mass of the group precipitated by ammonia, is concentrated in certain parts in proportion as the separation is effected.

I then ascertained that the portion containing titanium and analogous bodies showed radio-activity in the most marked degree, and after a very complicated process, on the nature of which I shall speak later, I obtained a substance a solution of which showed the principal analytical properties of titanium, but which emitted extremely active rays.

The radio-activity of a fraction of this substance has been roughly determined as being five thousand times greater than that of uranium. Further, this substance has chemical properties entirely different from those of radium and polonium.

The rays emitted by the new substance are quite comparable with those which have been observed by M. and Mme. Curie from polonium and radium.

These rays render gases capable of discharging electrified bodies, they excite phosphorescence in barium platino cyanide and affect photographic plates.

The new substance is distinguished from radium in that it is not spontaneously luminous, M. and Mme. Curie having shown that radium emits a perfectly distinct light when placed in a dark room.

I hope shortly to publish further researches on this radio-active material.—*Comptes Rendus*, No. 16, October 16th, 1899.

ON THE ELECTROLYSIS OF SOLUTIONS OF CHLORIDE OF ZINC, AND THE NATURE OF THE DEPOSITS OF SPONGY ZINC.

By F. FŒRSTER and O. GÜNTER.

STARTING from the hypothesis that the electrolytic deposition of spongy zinc is due to the presence of oxide of zinc precipitated on the cathode, the authors have made a certain number of experiments which confirm this supposition.

A zinc cathode was suspended in a perfectly pure neutral solution of chloride of zinc, containing 54·6 grms. of metallic zinc per litre. This cathode was placed between two anodes of pure electrolytic zinc.

With a current density of 1·4 ampères per square decimetre, a compact polished deposit of zinc was obtained for the first six hours, but after twenty hours spongy zinc was deposited, and the solution became cloudy on account of the presence of basic chloride of zinc in suspension.

On filtering off this precipitate, and replacing the old cathode by a fresh one, a good deposit was again obtained, but for a few hours only, when the electrolyte again became cloudy, and at the same time the deposit of zinc became spongy.

According to Schnabel ("Handbuch der Metallhüttenkunde," ii., p. 114), the formation of spongy zinc may be avoided by adding chlorine or chloride of lime to the electrolyte. The authors have tried the method described by Mylius and Fromm, which consists in keeping the solution of sulphate of zinc constantly acid. For this purpose they used two small anodes of platinum, from the surface of which they caused chlorine to be continually given off by connecting them with the positive pole of a battery consisting of two accumulators, while the negative pole was connected to the large zinc plate, which thus served as cathode for both pairs of anodes.

In neutral solution the above arrangement did not prevent the formation of spongy zinc.

The atmospheric oxygen easily oxidised the zinc in the presence of chloride of zinc, and a certain proportion of the oxide formed became dissolved in the electrolyte, giving basic chloride of zinc.

The formation of spongy zinc does not take place except when the excess of oxide commences to make the solution cloudy. If this precipitation is prevented by means of a periodical addition of hydrochloric acid, excellent deposits of zinc can be obtained. The authors, therefore recommend the addition of free hydrochloric acid to the electrolyte, in such proportion that the solution will be from $\frac{1}{10}$th to $\frac{1}{50}$th normal. In no case should it be allowed to become $\frac{1}{100}$th or $\frac{1}{500}$th normal.

By using a slightly acid electrolyte, and adopting the arrangement described above for giving off chlorine in the body of the solution, still better deposits are obtained. When the solution contains 0·2 grm. of free chlorine per litre, the hydrogen liberated at the cathode does not adhere to the electrode sufficiently long to affect the surface of the deposit.

But even when there is no doubt about the acidity of the mass of the solution, there arrives a time when spongy zinc is again deposited. This is due to the fact that the layer of the electrolyte in contact with the cathode loses its free acid; this inconvenience can, however, be remedied by keeping up a sufficient circulation of the solution.

The authors conclude by discussing the nature of the spongy zinc, and the effects obtained on adding certain

oxidising or reducing agents to the electrolyte. The addition of 1 per cent. of a perfectly neutral solution of persulphate of ammonium to a neutral solution of chloride of zinc enables very good deposits to be obtained. On the other hand, on adding 0·025 per cent of peroxide of hydrogen to the electrolyte, spongy zinc begins to form at the end of only ten minutes.—*Zeits. fur Elektrochemie*, v., [1], p. 16.

THE VOLUMETRIC ESTIMATION OF CARBON IN STEEL.

In a former paper (Chemical News, vol. lxxx., p. 52) the fact that combined and graphitic carbon separated from steel or pig-iron reacts best with respective mixtures of bichromate and sulphuric acid of definite percentage of sulphuric acid is briefly referred to. In amplification thereof the following tests were made :—

Combined Carbon.—The carbon was separated from 3 grms. of steel containing 1·18 per cent, and, after careful washing, was digested with 30 c.c. of a mixture of varying percentages of sulphuric acid and 0·7 grm. of dry powdered potassium bichromate. The digestions in the water-bath, made in batches of four, were stirred in rapid succession during a certain number of minutes. The asbestos filter and carbonaceous residue were sucked as dry as possible, but not otherwise dried. The results were as follows :—

	Percentage of carbon oxidised.	
Per cent H_2SO_4.	Digested thirty minutes.	Digested fifteen minutes.
10	0·58	—
20	0·77	—
30	0·90	—
40	1·05	—
50	1·17	1·04
60	1·19	1·12
70	1·20	1·08
80	1·10	0·81
90	0·59	—
100	0·35	—

Graphitic Carbon.—There is some difficulty in sampling a graphitic pig-iron so as to obtain concordant analytical results. Three results of assays made by the ordinary process gave 3·29, 3·47, and 3·16 per cent of graphite. This sample was sieved, and that portion retained which would pass through a 30 but not through a 60 mesh sieve. Three assays of this gave 1·45, 1·46, and 1·45 per cent graphite. As much of this sample as yielded graphite equal in weight to the combined carbon operated on was decomposed with nitric acid, and the residue treated as before with mixtures of bichromate and sulphuric acid. To facilitate comparison with the former series, the amount of graphite is calculated on to 3 grms., so that a complete combustion would give 1·18 per cent. The results were:—

Per cent H_2SO_4.	Carbon oxidised by digesting thirty minutes.
10	0·04
20	0·09
30	0·12
40	0·17
50	0·31
60	0·47
70	0·62
80	0·78
90	1·07
100	1·00

These results show that in combusting a carbonaceous residue by means of chromic and sulphuric acids the strength of the latter acid is a very important point; between 50 per cent and 70 per cent being most suitable for combined carbon and about 90 per cent the most suitable for graphite, although where higher temperatures are available the combustion of graphite may be speedily accomplished with the weaker acids.

Decomposition of Heated $K_2Cr_2O_7 + H_2SO_4$.—Mixtures of chromic and sulphuric acid are known to suffer decomposition at about 105° C. and beyond. Cross and Bevan point out that this reaction is more rapid in mixtures of bichromate and sulphuric acid than in mixtures of chromic anhydride and sulphuric acid, and they hazard the opinion that the portion of CrO_3 remaining undissolved is more liable to decomposition than that dissolved in the acid (*Journ. Chem. Soc.*, liii., 894). Mixtures of *bichromate* and sulphuric acid are decomposed slowly at 100° C., or even several degrees lower. The results with varying strengths of sulphuric acid are very irregular—first reaching a maximum, and then declining. As illustrating the limitations of the volumetric process, this is an important point. In the following experiments 0·7 grm. of powdered $K_2Cr_2O_7$ was digested with 30 c.c. H_2SO_4 of the stated strength. The figures show the percentage of the added bichromate estimated after heating at the indicated temperature for three hours.

Per cent H_2SO_4.	130° C.	120° C.	110° C.	100° C.	100° C. for sixteen hours.
30	100·0	—	—	—	—
40	100·1	—	—	—	—
50	100·1	—	—	—	99·9
60	98·6	99·2	99·6	99·9	99·0
70	91·3	98·2	99·0	99·6	97·6
80	88·7	95·1	96·5	98·1	88·7
90	91·3	95·8	96·8	98·2	92·6
100	94·8	—	—	—	97·6

In order to magnify the discrepancies obtained by heating for three hours at 100° C., a similar series were heated for sixteen hours (last column), when the small differences which might well have been due to experimental error turn out to be indications of a very slow decomposition. The results show that the decomposition is most energetic when the strength of sulphuric acid is about 80 per cent, and that 50 per cent to 60 per cent H_2SO_4 is the strongest acid permissible during prolonged heating. The conditions are not exactly those of a volumetric assay: there the reduction by the carbon rapidly lessens the amount of chromic acid and substitutes the corresponding amount of chromic sulphate; both these differences may favour the stability of the mixture. Although the perfectly stable solution made with 50 per cent sulphuric acid can accomplish, at the higher temperatures, all that is required in the particular branch of analysis being dealt with; many other strengths, even with three hours' digestion, introduce quite negligible errors when calculated into the few tenths or even units percentage of carbon metalliferous materials contain. Experiments in which the $K_2Cr_2O_7$ was retained as much as possible in the solid state gave results not appreciably different from similar experiments in which the $K_2Cr_2O_7$ was dissolved as far as possible; so that, for mixtures of $K_2Cr_2O_7$ and H_2SO_4, the state of the former reagents has little or nothing to do with the decomposition. Two other points repeatedly observed are that, after digestion, the cooled solutions deposited no crystals when the strength of H_2SO_4 was 50 per cent or less, or 80 per cent or more, but always in samples made up with the same volumes of 60 and 70 per cent H_2SO_4. The solubility, therefore, does not vary regularly with the strength of the sulphuric acid. In samples made up with 90 and 100 per cent H_2SO_4 the watch-glass was always covered with a solution of CrO_3, even when the digestions were made so far below the boiling-point of the mixture as 100° C. is. The volume of sulphuric acid used has very little influence on the speed of oxidation so long as enough is present to allow free movement of the carbon and filter in the oxidising mixture. This point was determined by digesting carbon from the previously used steel with equal amounts of $K_2Cr_2O_7$ and 30 and 60 c.c. of heated sulphuric acid for fifteen minutes at 100° C. The results were :—

Strength H_2SO_4. Per cent.	30 c.c.	60 c.c.
50	1·08	1·06
60	1·13	1·10
70	1·08	1·06

The results quoted in the former paper, nearly all of which were obtained by using 50 per cent H_2SO_4 solutions, are proof that no great loss is occasioned by CO being evolved along with the CO_2. No fear therefore need be entertained that in the ordinary moist combustion process, in which the CO_2 is absorbed and weighed, low results will be obtained on this account. Assuming that there is a trifling evolution of CO along with the CO_2, the mixture made with the weaker acid is about as likely to oxidise it as is the mixture made with the stronger acid, although neither at 100° C. or below would be very effective. Passed over heated CuO, a measured volume of CO yielded 0·0845 grm. of CO_2; passed steadily through a mixture made up with strong H_2SO_4, only 0·0020 grm. CO_2 was formed; with 70 per cent H_2SO_4, only 0·0016 grm.; and with 30 per cent H_2SO_4, only 0·0004 grm. As the carbon evolved as CO can be only 1 or 2 per cent of the total, the advantage of one strength of acid over another is not worth mentioning.

It is a matter of common experience that nickel crucibles are liable to become coated with soot, even in contact with non-luminous flames. As highly chromiferous materials are frequently opened up and otherwise manipulated in nickel vessels, these sooty deposits are a source of danger. Owing to the low atomic weight of carbon, a seemingly insignificant amount of soot would be disastrous if digested in an acid solution of chromic acid representing only a few decigrms. of the material.

J. T.

THE REACTION BETWEEN POTASSIUM CYANIDE AND METADINITROBENZENE.*

By W. R. HODGKINSON and Lieut. HOPE, R.A.

In the *Berichte* for 1884 is an abstract from *R. Trav. de Pharm.* (xxiii., 205, 235) of a communication by Lobry de Bruyn on the Action of KCN on *m*-Dinitrobenzene. The result of the action is stated to be an oxy-ethyl-nitrobenzonitrile (1.2.6). This reaction is also referred to in Beilstein's "Handbuch."

This reaction has been repeated with a slight modification.

In the abstract above noted it is stated that an alcoholic solution of the dinitrobenzene was treated with KCN dissolved in a little water. We have employed the purest KCN obtainable, and as nearly absolute alcohol as ordinarily possible.

On digesting for a little time (40 minutes to 1 hour) on a water-bath, we noticed the formation of the purple-red colouring-matter and its change into brown. On cooling, a considerable crystallisation took place. The solid was separated from the excess of alcohol, and was found to dissolve for the most part in hot water. A small amount of blackish amorphous substance remained insoluble.

On acidifying the water solution a brown precipitate was formed. It was washed with cold dilute sulphuric acid and water and then dissolved in hot alcohol, from which crystals were separated on cooling and also on evaporation.

On analysis (N_2 only) figures have been obtained pointing distinctly to a nitrocyanide or nitrile, $C_6H_5NO_2CN$. Considerably more than 80 per cent of the reaction has gone in this line.

The same body has been obtained with dry methyl alcohol and also with normal propylic alcohol as the solvents for the dinitrobenzene.

With acetone and paraldehyde as solvents, beyond the formation of a small amount of colouring-matter very little action could have taken place, for over 90 per cent of the dinitrobenzene was recovered and the KCN seemed scarcely acted on.

With an appreciable amount of water present and ordinary very alkaline cyanide the reaction probably runs quite differently.

With moderately dry and pure materials we have failed to obtain any sign of an oxy-ethyl or oxy-methyl derivative.

The nitrocyanide (or nitrile) forms brown needles from alcohol, which decompose (puff off) when heated to about 200°.

It does not seem to hydrolyse with KHO or on simply boiling with HCl.

We commenced this with a view of employing the oxy-ethyl mononitrile for another investigation, but now wish to re-investigate this reaction.

Ordnance College, Woolwich.

* Read before the British Association (Section B), Dover Meeting, 1899.

THE ACTION OF METALLIC MAGNESIUM ON WATER.

By EDWARD G. BRYANT, B.A., B.Sc. (Lond.).

THE references to this matter in chemical literature are, as far as I have been able to discover, very meagre and somewhat contradictory. The subject is dismissed in half-a-dozen words in most of the standard text-books, and I have not been able to find any account of original experiments. Yet it seems a point of some importance, as showing the relationship of magnesium to zinc on the one hand, and the alkaline earths on the other.

Gmelin's "Handbook" (Watts's translation, 1844), Watts's "Dictionary of Chemistry" (1892), and Dammer's "Handbuch der Anorganische Chemie," state that water does not decompose magnesium except at high temperature. Dammer gives Liebig and Bunsen as authorities, but I have not succeeded in finding any mention of the matter in the works of these two chemists.

On the other hand, Würtz's "Dictionary" says that magnesium slowly decomposes pure water, "l'eau pure," and that both carbonic acid and oxygen in the water accelerate the action. As far as oxygen is concerned, Gmelin supports this statement.

A chance experiment had led me to believe that the substances had a slight action on one another at ordinary temperatures, and the discovery of the above conflicting views induced me to carry out a series of observations as thorough as the means at my disposal permitted.

I find that magnesium and water react upon one another slightly at all temperatures; that the action depends very largely upon the amount of surface offered by the magnesium; that there is but slight difference in the amounts of gas evolved at boiling-point or in the cold; and that in all cases action ceases long before the magnesium has disappeared.

The magnesium used was the commercial metal, as I was quite unable to procure any in the pure state. Several samples were analysed qualitatively and one quantitatively; all, except one from Messrs. Johnson and Matthey, contained iron, with traces of zinc, aluminium, and calcium. The quantitative estimation of one sample gave:—

Iron	1·77 per cent.
Calcium	0·3 „

Messrs. Clowes and Caven found the best commercial metal pure enough for their experiments on the decomposition of copper sulphate; Villiers and Borg, also (CHEM. NEWS, lxviii., 263), speak of the high degree of

purity of ordinary magnesium. I further tested the metal for carbon, but without result; it dissolved perfectly in nitric acid, giving a colourless solution; also when dissolved in hydrochloric acid, and the gas evolved passed over pure copper oxide, no trace of carbon dioxide could be obtained. The results obtained from the various specimens when placed in water were indistinguishable whether iron were present or not.

The decomposition can be seen without the least difficulty by placing a few magnesium filings in a tube filled with water, and then inverting the tube in a small vessel of water. The powder is seen to become more and more flocculent, and after a few seconds the whole mass rises to the top. If it be shaken down a bubble of gas is left behind; masses of the filings keep rising and falling, and small bubbles ascend rapidly for some time. The action slackens after a few minutes, but abundant bubbles can be obtained by occasional shaking, even after an hour or two, and for many hours the action continues with continually less energy. The gas is pure hydrogen; on exploding with oxygen in excess, no trace of carbon dioxide could be found. The solution gives a strong alkaline reaction with phenolphthalein, and will usually give a cloudiness with ammonia and sodium phosphate. I could never find any calcium in solution. From 0·1 grm. of powder in 100 c.c. water, 2 to 3 c.c. of hydrogen can be obtained; from the same amount of metal, in 550 c.c. of water, 5·5 c.c. of hydrogen. On the basis of these figures the solubility of magnesium oxide in water can be roughly determined, and is found to be 1 part in 225,000 of water. If ribbon be used instead, the yield of gas is not more than one-fourth as much for the same amounts of metal and water. The colour of the metal is decidedly brownish-white after the experiment, and its lustre is greatly diminished. The water, if cold, never becomes clouded in the least degree, even after rapid shaking.

If the ribbon be cleaned with sand-paper (or the powder with 1 per cent HCl and thoroughly washed), the action re-commences on putting it back into the same water, much as at first, and this can be repeated as long as any metal remains; or, as a variation, an additional quantity of magnesium can be added to the water with like result.

Certain neutral salts, especially sodium sulphate, cause a much stronger action to take place, the yield of gas being three or four times as great. The solution also gives a much stronger precipitate of the ammonic magnesium phosphate. Alcohol, on the other hand, has not the slightest effect on the metal until about 25 per cent of water has been added to it.

Magnesium powder placed in alcohol remains bright and inactive. If a quantity of water be added action starts, and can be renewed by the addition of more water. Lastly, if a few crystals of sodium sulphate be introduced, a much stronger action will commence almost immediately.

It is noteworthy that alcohol will not dissolve enough magnesium oxide to give a trace of colour with phenolphthalein; water dissolves enough to give a very faint precipitate with ammonic phosphate and ammonia, while saturated sodium sulphate solution will give a very distinct precipitate.

Water dissolves such an inappreciable quantity of the oxide that the difference between the amounts of gas given with pure water and water saturated with the oxide, is, as might be expected, hardly measurable with ordinary apparatus. The difference in the case of sodium sulphate treated in the same way ought to be much larger, but I could not obtain the expected amount.

The action of magnesium on boiling water is more rapid, but is more quickly ended, the amount of gas evolved being very little larger than when cold water is used. The water and the containing vessel present a filmy white appearance when cold, as if a slight deposit of oxide had occurred.

The possible influence of gases and other impurities in the distilled water used was carefully examined. In the first place, the quantity of gas evolved was proved to be almost exactly proportional to the amount of magnesium present, the volumes of water being equal. To make certain of the point, some water was re-distilled from alkaline permanganate, and before it had cooled was placed in a small flask and boiled. Some magnesium powder was placed in a second flask connected to the other by a glass tube. Carefully washed and dried coal-gas was passed over the magnesium and the boiling water. The magnesium was heated to 200° C. for half-an-hour, and the water kept boiling for the same time. The two end-tubes of the flasks were then instantly connected together, so that no oxygen could enter as the apparatus cooled. When cold, the water was poured over the magnesium. A brisk action started at once, and continued for the usual length of time. The experiment was repeated twice: (1) without heating the magnesium, (2) in pure hydrogen instead of coal-gas, as the latter might possibly have introduced some oxygen, but no difference could be detected in the action.

These experiments seem to prove conclusively that the oxygen or other gas in the water is not essential to the action. Since magnesium containing no carbon and no iron can decompose water, copper, silver, and other electro-negative metals being also absent, an electrical couple is also out of the question. Finally, no calcium could ever be detected in the solution, and the amount present in the magnesium is not sufficient to cause the evolution of more than a fraction of the hydrogen found. Magnesium has itself, I submit, the power to decompose water at all temperatures above 0° C., and the action is stopped by an insoluble coating of oxide forming on the metal. This would explain the change of colour seen after the action has ceased, the renewal of action when the surface is cleaned, and the more abundant evolution of gas from a solution of sodium sulphate, since magnesium oxide is more soluble in that than in pure water. I have not yet attempted to prove the presence or absence of a film of hydrogen on the metal in addition to the oxide. A film of this kind is well known in the case of zinc and sulphuric acid, and has been stated to form on aluminium (A. Ditte, *Comptes Rendus*, Dec. 5, 1898).

In conclusion, I wish to acknowledge my indebtedness to Prof. Smithells, for much help towards carrying out the experiments.

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LIQUID AIR AS AN ANALYTIC AGENT.*

By Professor DEWAR, M.A., LL.D., F.R.S.

(Concluded from p. 202).

Photographic Action at the Temperature of Liquid Air.

IN a former lecture on "Phosphorescence and Photographic Action," it was shown that photographic action was reduced by 80 per cent at the temperature of −182° C. It was further proved that a sensitive film was still com-

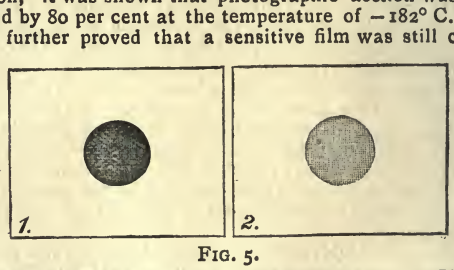

FIG. 5.

1, Photographic film exposed at ordinary temperature. 2, Photographic film cooled in liquid air during exposure. Both were exposed for the same length of time, and both were developed together.

* A Lecture delivered before the Royal Institution of Great Britain, April 1, 1898.

paratively active at the temperature of −210° C. Experiments in this direction have been continued at different times.

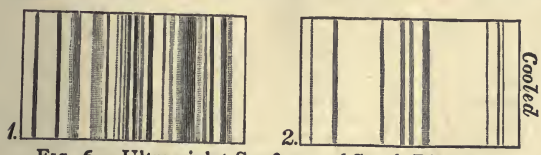

FIG. 6.—Ultra-violet Spectrum of Spark Discharge.

1, On film at ordinary temperature. 2, On film cooled in liquid air. Both exposed for the same length of time, and then developed together.

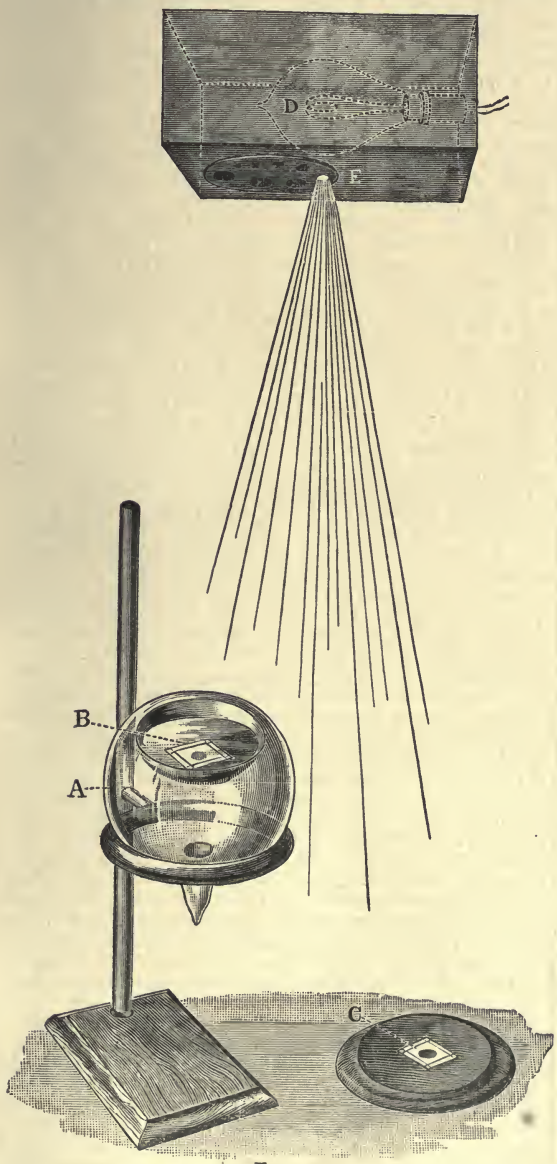

FIG. 7.

A, Vacuum cup with liquid air, into which is placed a photographic film in a small metallic slide having a hole in the centre. C, A metallic slide, holding a photographic film, which is exposed at ordinary temperature. Both of these are exposed to the light from a 16 candle-power lamp, D, contained in a box. The light is diminished or increased by the diaphragm at E.

In these new experiments the source of light was respectively a 16 candle-power lamp, a magnesium and cadmium spark discharge, and a Röntgen bulb. Small dark slides were prepared having a circular hole. One was placed in liquid air, and another simultaneously exposed for the same time at the ordinary temperature (FIG. 7). They were developed together, and the density of the image observed (Fig. 5).

Distance of Plates from Source of Light giving the same Photographic Intensity.

Source of light.	Cooled plate.	Uncooled plate.	Ratio of intensities at balance.
	In.	In.	
16 candle-power lamp	20	50	1 to 6
Ultra-violet spark magnesium and cadmium	22½	90	1 to 16
Röntgen bulb	10	24¾	1 to 6

Further trials were made by bringing the cooled plate nearer to the source of light until finally a position was found where the very feeble photographic impression that appeared on both plates had the same density. In this position the relative distances of the plates from the source of light were measured. This mode of conducting the photographic comparison of the hot and cold plates gets over the difficulty of variation in the intensity of the source of light. From these experiments it would appear that when cooled to the temperature of liquid air both the incandescent lamp and the Röntgen radiation were reduced to 17 per cent of their photographic action at the ordinary temperature; whereas the ultra-violet radiation was reduced to about 6 per cent. This marked increase in the inertia of the photographic plate at low temperatures for the short-wave lengths cannot be explained by the absorption of liquid air, for such radiation as this is small for a thickness of 10 to 20 m.m. of the liquid. It is possible that the ultra-violet radiation is dissipated by the photographic film at low temperatures to a greater extent than with ordinary light, through absorption and subsequent emission as a phosphorescent glow. It would seem probable that if the plate could be developed at these low temperatures no action would be apparent, and that it is during the heating up after the low temperature exposure that the photographic action on the film takes place through an internal phosphorescence. This possibility must make us cautious in drawing inferences as to possible chemical action at low temperatures.

A more elaborate study of photographic and phosphorescent effects at low temperatures would add much to our knowledge of the chemical and physical actions of light.

THE DEFINITION OF THE ELEMENT.*

By F. P. VENABLE.

(Concluded from p. 207).

THERE is no field of mental activity requiring more faith than tnat of the chemist. He is dealing with the "evidences of things unseen." He must not be content with the mere gathering of facts, but divine what he can of their deeper meaning. Few chemists have had such insight as Graham into the significance of even the simplest changes. He was not content with mere surface observation. Even the commonest observed phenomena were to him full of meaning as to the atoms and their "eternal motion." Thorpe ("Essays in Historical Chemistry," p. 219) has drawn afresh the attention of the chemist to the thoughtful words of this great thinker. His mind was filled with the fascinating dream of the

* Address of the Vice-President before Section C—Chemistry—of the American Association for the Advancement of Science, at the Columbus Meeting, August, 1899.

unity of matter. "In all his work," says Adam Smith, "we find him steadily thinking on the ultimate composition of bodies. He searches after it in following the molecules of gases when diffusing; these he watches as they flow into a vacuum or into other gases, and observes carefully as they pass through tubes, noting the effect of weight, of composition, upon them in transpiration. He follows them as they enter into liquids and pass out, and as they are absorbed or disolved by colloid bodies; he attentively inquires if they are absorbed by metals in a similar manner, and finds remotest analogies which, by their boldness, compel one to stop reading and to think if they really be possible.

In his paper entitled "Speculative Ideas respecting the Constitution of Matter," published in the *Proceedings of the Royal Society* in 1863, which Thorpe calls his "Confession of Faith," he tells of his conception that these supposed elements of ours may possess one and the same ultimate or atomic molecule existing in different conditions of movement.

It is not possible for me, in the limits of this Address, to array before you all of the various evidence which leads to the belief that our so-called elementary atoms are after all but compounds of an intimate peculiar nature whose dissociation we have as yet been unable to accomplish. When properly marshalled, it gives a very staggering blow to the old faith. Thorpe speaks of the "old metaphysical quibble concerning the divisibility or indivisibility of the atom." To Graham "the atom meant something which is not divided, not something which cannot be divided." The original indivisible atom may be something far down in the make-up of the molecule.

How shall the question as to the composite nature of the elements be approached? The problem has been attacked from the experimental side several times during the last half century, but the work seems to have been carried on after a desultory fashion and was soon dropped, as if the workers were convinced of its uselessness. The results, being negative, simply serve to show that no method was hit upon for decomposing the elements upon which the experiments were performed. Thus, for instance, Despretz performed a number of experiments to combat Dumas' views as to the composite nature of the elements. Despretz made use of the well-known laboratory methods for the separation and purification of substances. Such were distillation, electrolysis, fractional precipitation, &c. Such work was quite inadequate to settle the question, as Dumas had pointed out that unusual methods must be used, or, he might have added, the old methods carried out to an unusual or exhaustive extent. Certainly, if a moderate application of the usual methods was sufficient for this decomposition, evidences of it would have been obtained long ago by the host of careful workers who have occupied themselves over these substances. Crookes has busied himself with the method of fractional precipitation (though not with special view to the testing of this question), and applied it most patiently and exhaustively to such substances as the rare earths, without obtaining results from which anything conclusive could be drawn. Victor Meyer seems to have believed that the decomposition could be effected by high temperatures, and was very hopeful of experiments which he had planned before his untimely death. Others have spasmodically given a little time to the problem, but no one has thought highly enough of it to attack it with all of his energy.

Let us stop a moment and ask ourselves what would be attained if any one should succeed in decomposing an element by one of the usual methods. Has not this been done repeatedly in the past and merely served to add to the list of the elements? Didymium has been made to yield praseo and neodymium. That which was first called yttrium has been divided into erbium, terbium, and ytterbium, and according to Crookes may possibly be still further decomposed. But these and similar decompositions are not generally accepted as offering any evidence that elements can be decomposed. It is merely the discovery of one or more new substances which have remained hidden in constant association with known bodies which were supposed to be simple. It would be necessary to prove that a single individual element had, by the process adopted, been actually decomposed and not some pre-existing impurity discovered. This, of course, would be exceedingly difficult, and all such attempts as those mentioned can have little bearing upon the general question, and can hold out slight hope of reward beyond the fame springing from the discovery of a new element.

Successful decomposition should mean much more. It should mean the discovery of a method which will decompose not one, but many, or indeed all of the elements, and the decomposition of these must not yield a larger number of supposedly simple bodies, but a small group of one or two or three which are common constituents of all. It is quite idle to venture upon any prediction whether such a method will ever be discovered. Setting aside, then, the direct experimental proof of the composite nature of the elements as unattainable at present, let us next examine the indirect evidence. It would seem wisest for the present to introduce under that heading the spectroscopic work of Lockyer. The results, while highly interesting, are too indefinite as yet to speak of as having a direct bearing. Yet a careful study of the spectra of the elements leads us to a strong suspicion that the less plausible assumption is the one that the particles which give rise to such varied vibrations are simple and unitary in nature. Lockyer's most recent work, following up the line of his "Working Hypothesis" of twenty years ago, is very suggestive, and may lead to important results ("Chemistry of the Hottest Stars," *Roy. Soc. Proc.*, lxi., 148; "On the Order of Appearance of Chemical Substances at Different Temperatures," CHEM. NEWS, lxxix., 145). Still too much must be assumed yet for such work to be very conclusive. He writes of "proto-magnesium and proto-calcium," and Pickering discusses a "new hydrogen," all with an assurance and confidence which proves at least how deeply these changes in the spectra have impressed some of those who have most deeply studied them.

But a more important method of indirectly testing the question is through a comparison of the properties of the atoms. Such a comparison has been made as to the atomic weights. In other words, the idea of the composite nature of the elements followed very closely upon the adoption of a stricter definition of them as simple bodies. Dalton, Prout, Döbereiner, Dumas, Cooke, and many others, have aided in developing the idea, sometimes faultily and harmfully, at other times helpfully. Some fell into the common error of going too far, but all were struck by the fact that when these combining numbers, or atomic weights, were compared, strange and interesting symmetries appeared. The times were not ripe for an explanation of their meaning, and such crude assumptions as that of Prout, that the elements were composed of hydrogen, or that of Low, that they were made up of carbon and hydrogen, were too baseless to command much genuine support or to withstand much careful analysis. The important feature of agreement between such theories was the belief that the elements were composite and had one or more common constituents.

From the comparison of one property, the atomic weights, the next step was to the comparison of all the properties. This comparison is brought out clearest and best for us in the Periodic System. Here all the properties are very carefully tabulated for us. The study of the system leads indisputably to the conviction that this is not an arbitrary, but a natural arrangement, exceedingly simple in its groundwork, but embodying most fascinating symmetries, which hint of great underlying laws. He who looks upon it as a mere table of atomic weights has lost its meaning. It tells, with no uncertain note, of the kinship of the elements, and leads to a search after the secret of this interdependence and of their common factor

or factors. There is so much which is made clearer if we assume a composite nature for the elements that many do not hesitate to make the assumption.

Still another indirect method of approaching that problem is by analogy with bodies whose nature and composition are known. A very striking symmetry is observed between the hydrocarbons, and these in the form of compound radicals show a strong resemblance to certain of the elements. This analogy need not be dwelt upon here. It has been recognised for a long time, and tables of hydrocarbons have been constructed after the manner of the Periodic System. Now these bodies are simply built up of carbon and hydrogen in varying proportions, and in any one homologous series the increments are regular. We know that they are composite, and that they have but two common factors, carbon and hydrogen.

Again, the fact that certain groups of associated atoms behave as one element and closely resemble known elements may be taken as a clue to the nature of the elements. Thus carbon and nitrogen, in the form of cyanogen, behave very much like the halogens; and nitrogen and hydrogen in the form of ammonia so closely resemble the group of elements known as the alkalis that this "volatile alkali" was classed with them before the era of our elements and the analogy led to a vain search for an "alkalising principle," and later to an equally futile pursuit of the metal ammonium.

A further clue to this nature is afforded in the remarkable changes of properties which can be brought about in some elements by ordinary means, and one might mention the equally remarkable veiling of properties induced by the combining of two or more atoms. Thus copper exists in a cuprous and a cupric condition, and the change from one to the other can be readily brought about. And this is true of many other elements.

This has doubtless been a tedious enumeration to you of well-known facts and arguments, but it has been necessary, for I wish to lead you to the summing-up of these arguments and to induce you to draw boldly the necessary deductions. It is high time for chemists to formulate their opinions in this matter. It would seem as if we were shut up to one or two conclusions. Either these imagined simple bodies are after all compounds, built up of two or more common constituents, or they are but varying forms of one and the same kind of matter subjected to different influences and conditions. The supposition that they are distinct and unrelated simple bodies is, of course, a third alternative, but to my mind this is no longer tenable.

The second hypothesis is the one put forth by Graham. It was his cherished vision of the gaseous particles about which he thought so deeply, and in many ways so truly. Thorpe has written of this as follows (*loc. cit.*, 222):—

"He conceives that the various kinds of matter, now recognised as different elementary substances, may possess one and the same ultimate or atomic molecule existing in different conditions of movement. Graham traces the harmony of this hypothesis of the essential unity of matter with the equal action of gravity upon all bodies. He recognises that the numerous and varying properties of the solid and liquid, no less than the few grand and simple features of the gas, may all be dependent upon atomic and molecular mobility. Let us imagine, he says, one kind of substance only to exist—ponderable matter; and, further, that matter is divisible into ultimate atoms, uniform in size and weight. We shall have one substance and a common atom. With the atom at rest the uniformity of matter would be perfect. But the atom possesses always more or less motion, due, it must be assumed, to a primordial impulse. This motion gives rise to volume. The more rapid the movement, the greater the space occupied by the atom, somewhat as the orbit of a planet widens with the degree of projectile velocity. Matter is thus made to differ only in being lighter or denser matter. The specific motion of an atom being inalienable, light matter is no longer convertible into heavy matter. In short, matter of different density forms different substances—different inconvertible elements, as they have been considered."

The hypothesis that the elements are built up of two or more common constituents has a larger number of supporters and would seem more plausible. Some have supposed one such primal element by the condensation or polymerisation of which the others were formed. Thus we have the hydrogen theory of Prout, modified to the one-half atom by Dumas, and finally by Zängerle to the one-thousandth hydrogen atom. The suggestion of Crookes as to the genesis of the elements from the hypothetical protyle, under the influence of electricity, may also be mentioned here.

Others have adopted the supposition of two elements, Reynolds making one of these an element with a negative atomic weight, whatever that may mean. Low and others have fixed upon carbon and hydrogen as the two elements.

There are many practical difficulties in the way of these suppositions; the lack of uniformity in the differences between the atomic weights, the sudden change of electro-chemical character, and the impossibility, so far, of discovering any law underlying the gradation in the properties of the elements with the increase of atomic weights, are some of the difficulties. In comparing these two hypotheses that of Graham seems to me very improbable. I have thought of valence as dependent upon the character of the motion of the atom, but cannot well conceive of a similar dependence of atomic weight and all the other properties. There remains, then, the hypothesis of primal elements by the combination of which our elements have been formed. These molecules are probably distinguished from the ordinary molecules by the actual contact and absolute union of the component atoms without the intervention of ether.

Since these elemental molecules cannot as yet be divided, we may retain the name atom for them, but the idea of simplicity and homogeneity no longer belongs to them. The definition of an element as a body made up of similar atoms is equally lacking in fidelity to latest thought and belief, but chemists would scarcely consent to change it, and, indeed, it may well be retained, provided the modified meaning is given to the word atom. But, after all, an element is best defined by means of its properties. It is by close study of these that we decide upon its elemental nature, and through them it is tested. Complete reliance can no longer be placed upon the balance and the supposed atomic weight.

All elements are acted upon by gravity and chemical force and other physical forces, but within the last few years certain gaseous elements have been discovered which are not influenced by chemical force or affinity. According to some (Piccini, *Zeits. An. Chem.*, xix., 295) this necessitates a division of the elements into two classes. Manifestly, since it is chiefly by the action of chemical force that we study the elements, the absence of such action cuts us off from our chief means of finding out anything about them, and it is equally clear that bodies so diverse cannot well be classified together. If all attempts at bringing out the chemical union of these gaseous elements with other bodies fail, I believe that we should insist upon the existence of two classes of elements, and keep them distinct in all comparisons.

Of course we are quite at a loss to say just what chemical force is, but it is believed to be determined by the electrical condition of the atom. Thus we have the elements which show the action of chemical affinity varying from strongly electro-positive to strongly negative. This electrical charge of the atom seems to be a primitive, inherent property, and so beyond our control or power to change. At least no change of the kind has ever been recognised and recorded. Sodium remains positive and chlorine negative, in spite of all that may be done to them. We can, by uniting the two temporarily, cloak and neutralise

their opposite natures, but the original condition returns on their release.

Is it not fair to assume that argon, helium, and their companion gases, having no affinity, are without electrical charge—atoms from which the electrical charge has been withdrawn; the deadest forms of inanimate matter? Were they thus without electro-chemical properties and affinity from the beginning, or did they start out as ordinary atoms (if I may so call them), and somehow, somewhere lose these properties, and with them the power of entering into union of any kind, even of forming molecules, doomed to unending single existence? Can these be changed atoms of some of our well-known elements, a step nearer to the primal elements and with the electrical charge lost? Is it possible for us to bring about these changes? May we not unwittingly have done so at some time or other in the past? Is it possible to restore the electrical charge to such atoms, and so to place them once more on a footing of equality with elements of the conventional type? These and many other questions surge through the mind as one thinks of these wonderful gases. Perhaps the coming century will unfold the answers.

PHOTO-CRYSTALLISATION.*

By FERDINAND G. WIECHMANN, Ph.D.

Light is one of the forms taken by the radiant energy which emanates from the sun. It is well known that light—or possibly some other form of energy accompanying light—is able to bring about about chemical and physical changes.

The influence of sunlight on sugar solutions has been noted at various times and by different observers. The earliest reference to an instance of this kind seems to be contained in an article published by Dr. C. Scheibler in 1861-62 in the *Jahresbericht über die Untersuchungen und Fortschritte auf dem Gesammtgebiete der Zuckerfabrikation*, vols. i. and ii., p. 194.

Some years ago the present writer noticed an interesting case of photo-action. A solution of partially inverted sucrose was, under the influence of sunlight, transformed into a crystalline solid. This change in the state of aggregation was accompanied by chemical change; the original amount of invert sugar in the solution, 84·8 per cent, was increased to 97·06 per cent. A memorandum of this observation was published at the time (*School of Mines Quarterly*, vol. xiii., No. 2), and as the matter seemed to warrant further and more careful study, after some preliminary trials, a series of experiments was planned and commenced in December, 1891. The observations then begun have extended over a period of four years, and a record of the work done is herewith given. In this connection it is a pleasant duty to acknowledge the valuable services of Mr. Edward C. Brainerd, to whom the writer is indebted for the analytical data presented.

The term photo-crystallisation, under which this article appears, has been coined by the writer because this word seemed to indicate most accurately the nature and character of the phenomena studied.

Photo-crystallisation has been observed in solutions of sucrose, partially inverted, and in plates of solid (barley) sugar. This communication will, however, deal only with the investigation of the sucrose solutions. These sucrose solutions were made by dissolving 64 parts by weight of perfectly pure sucrose (polarisation 100) in 16 parts by weight of distilled water; this gave an 80 per cent solution.

Partial inversion of this sucrose was effected by chemically pure hydrochloric acid, of specific gravity 1·20. Of this, an amount was used equivalent to 0·025 per cent of the weight of the dry sucrose employed, and equivalent to 0·02 per cent of the weight of the solution.

* *School of Mines Quarterly*, vol. xvii., No. 4.

Table I.

Series I.—*Exposed to Direct Sunlight.*

State of crystallisation after — days.	Specimen numbers. 1. 90·9. Acid.	2. 90·9. Neutral.	3. 80·6. Acid.	4. 80·6. Neutral.	5. 58·0. Acid.	6. 58·0. Neutral.
100	A	D	B	C	E	F No crystals.
135	Solid.	B	A	B	B	C No crystals.
170	..	B	A	B	B	C No crystals.
225	..	B	Solid.	C	A	D No crystals.
324	..	Solid.	..	Solid.	A	B Two small crystals.
365	..	..	..	..	Solid.	A Seven small crystals.
531	..	..	..	..	..	A Crystals throughout liquid. About ⅛ of bottom of flask covered thinly by crystals.
628	..	..	..	..	..	A Crystals a through solution.
785	..	..	..	..	..	A Ditto.
1095	..	..	..	..	..	A Ditto.
1473	..	..	..	..	..	A Crystals al through mass. A semi-solid magma.

The solutions thus prepared contained inverted sucrose to the extent of—

Solution A = 90·9 per cent
„ B = 80·6 „
„ C = 58·0 „

Each of the three solutions was divided into halves, thus giving rise to—

Solutions A I., A II.
„ B I., B II.
„ C I., C II.

Solutions A I., B I., C I. were left as prepared, very slightly acid; Solutions A II., B II., C. II. were carefully neutralised with sodium bicarbonate, methyl-orange being the indicator used.

These solutions were placed into eighteen white glass flasks, which were securely corked after introduction of the solutions. They were divided into three groups, each

TABLE II.

SERIES II.—*Exposed to Diffuse Daylight.*

State of crystallisation after — days.	Specimen numbers. 7. 90·9. Acid.	8. 90·9. Neutral.	9. 80·6. Acid.	10. 80·6. Neutral.	11. 58·0. Acid.	12. 58·0. Neutral.
100	A	E	B	D	C	F No crystals.
135	A	E	B	D	C	F No crystals.
170	A	E	B	D	C	F Two small crystals.
225	A	E	B	D	C	F Ditto.
324	A	E	D	C	B	F Ditto.
365	B	E	D	C	A	F Ditto.
531	B	D	C	A	A	E About thirty crystals on bottom of flask.
628	B	C	D	Solid.	A	E
785	A	A	B	..	Solid.	C Fine crystals all through the solution.
1095	Solid.	..	A	..	..	B Crystals all through solution, and layer of crystals on bottom ½ inch thick.
1473	..	..	A	..	..	B Crystals all through the mass; semi-solid.

TABLE III.

SERIES III.—*Kept in Darkness.*

State of crystallisation after — days.	Specimen numbers. 13. 90·9. Acid.	14. 90·9. Neutral.	15. 80·6. Acid.	16. 80·6. Neutral.	17. 58·0. Acid.	18. 58·0. Neutral.
100	E	C	A	B	D	F No crystals.
135	E	D	A	B	C	F No crystals.
170	E	D	A	B	C	F No crystals.
225	E	D	A	C	B	F No crystals.
324	E	C	A	D	B	F No crystals.
365	E	C	A	D	B	F One crystal.
531	D	B	A	C	B	E Six crystals on bottom.
628	E	B	A	D	C	F
785	D	A	B	C	C	E
1095	C	Solid.	A	B	B	D A few crystals on bottom, all the rest is liquid.
1473	D (*a*)	..	A (*b*)	C (*c*)	B (*d*)	E Ditto.

(*a*) Half solid; liquid colour of amber.
(*b*) Almost solid.
(*c*) Nine-tenths solid; liquid of pale amber colour.
(*d*) Very nearly solid. Sides hard, central portion a magma.

group consisting of the following six specimens, which contained respectively:—

Inverted sucrose	90·9	per cent	Slightly acid.
,, ,,	90·9	,,	Neutralised.
,, ,,	80·6	,,	Slightly acid.
,, ,,	80·6	,,	Neutralised.
,, ,,	58·0	,,	Slightly acid.
,, ,,	58·0	,,	Neutralised.

The three sets were numbered respectively from 1—6, 7—12, 13—18. Set 1—6 was exposed to direct sunlight, as far as the condition of the laboratory in which the work was done permitted; exposure of the laboratory was south-west. Set 7—12 was placed in diffuse daylight, but shielded from all direct sunlight. Set 13—18 was kept in a dark closet, from which, however, diffuse daylight was not absolutely excluded during all of the time, as the door had occasionally to be opened to remove articles from or place articles into the closet; still, practically, it was kept in darkness. These three sets were under continuous observation, and the accompanying tables show the manner in which crystallisation progressed in the solutions.

The letters A, B, C, D, E, F employed in the tables are intended to indicate only the *relative* extent to which crystallisation had advanced in any given set of specimens at the time when the observation was made. The letters of one series cannot be compared directly with those of another series, nor taken as expressing that the same degree of crystallisation had been attained in both series. Wherever, however, one and the same letter is used for more than one specimen in the *same* series, this signifies that crystallisation had advanced to an equal degree in the specimens thus marked.

Although the time of growth of the crystals in the various solutions differed greatly, the manner of growth was the same in all cases. The first crystals made their appearance in the body of the solution and settled to the bottom of the flask. Then the crystals began to grow upwards on the sides of the flask, the interior portion of the solution remaining fluid the longest.

The growths consisted of snow-white crystalline nodules, which, through aggregation, gave rise to fern-like forms.

(To be continued).

Synthesis of Alcohol.—M. Berthelot.—The author confirmed previous theoretical considerations when he proved experimentally the regeneration of alcohol by means of pure olefiant gas, and showed that the body obtained has the same physical and chemical properties of ordinary alcohol. This was confirmed still more definitely by the direct synthesis of compounds of olefiant gas with the hydracids—that is to say, hydrochloric, hydrobromic, and hydriodic ethers—and from this he has devised a general method for the synthesis of derived alcohols and all the carbides of the same series. Finally, the direct synthesis of acetylene from the elements carbon and hydrogen, then the synthesis of olefiant gas from acetylene, has enabled the author to effect experimentally the complete synthesis of alcohol from the elements.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 8.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 27th, 1899.

Prof. W. E. AYRTON, F.R.S., Vice-President, in the Chair.

DR. S. W. RICHARDSON read a paper "*On the Magnetic Properties of the Alloys of Iron and Aluminium.*"

Observations were made upon four alloys containing respectively 3·64, 5·44, 9·89, and 18·47 per cent of aluminium. The alloys were used in the form of anchor rings, and were wound with primary and secondary coils separated by asbestos paper. The temperatures used ranged from −83° C. to 900° C. The low temperatures were produced by the rapid evaporation of ether, surrounded either by ice and salt or by carbon dioxide snow. The high temperatures were obtained either electrically or by gas muffles. In both cases the actual temperatures were deduced from the resistance of the secondary, which was made of platinum wire and wound next the metal. The author employed Maxwell's null method of measuring mutual induction, increasing the sensitiveness by the introduction of a secohmmeter making about three revolutions per second. In order to test the accuracy of the method some of the experiments were repeated with a ballistic galvanometer in the ordinary way, and the agreement obtained between the results in the two cases was well within the limits of experimental error. The chief conclusions to be drawn from the experiments may be summed up as follows:—(1). The alloys behave magnetically, as though they consisted of two distinct media superposed. (2). The general roundness of the curves and their lack of abruptness near the critical point seems to indicate that the alloys are heterogeneous in structure. (3). The permeability decreases with rise of temperature near the critical point until a minimum value is reached, when further rise of temperature produces very slight diminution, if any, in the permeability. (4). The experiments suggest that the maximum value of the permeability for an alloy containing 10 per cent of aluminium is reached at about −90° C. (5). An alloy containing 18·47 per cent of aluminium has a critical point at about 25° C. and gives no indication of temperature hysteresis. This alloy probably has a maximum permeability much below −90° C. The author has found that at high temperatures there is a second maximum in the induction curve. This maximum becomes less and less noticeable as the field is increased.

The SECRETARY read a note from Prof. BARRETT "*On the Electric and Magnetic Properties of Aluminium and other Steels.*" The first part of the note dealt with the electrical conductivity of various alloys, and discussed the effect of composition and annealing upon the value of the conductivity. The second part of the note referred to magnetic effects. The most remarkable effect produced by aluminium on iron is the reduction of the hysteresis loss. The permeability of nickel steels is shown to be very much influenced by annealing. It is found that the addition of a small quantity of tungsten to iron hardly affects the maximum induction, yet increases the retentivity and coercive force. The experiments show that the best steel for making permanent magnets is one containing 7½ per cent of tungsten. The magnetometric method was employed throughout.

Prof. S. P. THOMPSON drew attention to the wide range of temperature over which the author had conducted his experiments, and also to the small number of alloys used. He said a very much finer connection between the properties could be obtained from the examination of more alloys, and expressed his interest in the existence of the second maximum on the induction curve. He would like to know how the percentage composition of the alloys had been determined. Turning to Prof. Barrett's note, Prof. Thompson referred to the difference in the breadths of the hysteresis curves for aluminium and chromium alloys.

Mr. APPLEYARD asked for information upon the permanence of the curves.

Dr. RICHARDSON, in replying, said the compositions were determined by analyses made after the experiments had been performed. It was proposed to carry on the research upon a series of aluminium alloys which he had obtained.

The CHAIRMAN expressed his special interest in the agreement which the author had obtained between the ballistic method and the null method of Maxwell, increased in sensitiveness by the secohmmeter.

Mr. ADDENBROOKE exhibited a Model illustrating a number of the Actions in the Flow of an Electric Current. The model consisted of a spiral of steel wire in the form of a closed circuit. Inside the spiral was placed a wire which was supposed to be carrying the current, and which directed the motion of the spiral. A rotational movement given to one part of the spiral was transmitted by the wire and produced a rotational movement at another part of the spiral. The resiliency of the spring represents capacity, and the torque electromotive force. Self-induction can be represented by weighing the spring.

Prof. EVERETT expressed his interest in the way that the correspondence between the propagation and the rotation agreed with that between the direction of a current and the direction of the magnetic force.

Prof. S. P. THOMPSON agreed that many analogies could be worked out by the model, but gave one or two examples to show that erroneous conclusions might be drawn by pushing the analogy too far.

Mr. W. WATSON repeated some Experiments with the Wehnelt Interrupter devised by Prof. Lecher. The experiments showed, in a clear and striking manner, the fact that subsequent sparks tend to pass through the portion of air heated by the first one. In the first experiments motion of the heated air was caused by differences in density, and in the later experiments by allowing the sparks to take place in a strong electro-magnetic field. The continuous rotation of the spark in a given field proved the unidirectional nature of the discharge. In reply to Mr. Blakesley, Mr. Watson said he used the word "ionised" in his explanations to express simply the fact that the air had been rendered a conductor by the passage of the spark.

The CHAIRMAN referred to one of the first experiments performed. In this experiment the electrodes consisted of two copper wires in a vertical plane, slightly inclined to one another, and nearest together at their lowest points. On switching on the current the spark passed between the lowest points, but as the ionised air ascended so did the most conducting path, and consequently the spark worked its way to the top of the electrodes. Here the heated air passed away, and the spark returned to the lowest point to rise again. The Chairman thought that these effects might be due to the magnetic force produced by the circuit itself. That similar effects in the arc light were due to this cause had been proved many years ago.

Mr. WATSON repeated some of the experiments under new conditions, and proved that the explanation of the phenomena was not to be found in the tendency of the circuit to enlarge itself owing to magnetic forces.

Mr. BOYS pointed out that the relation of the heating effect to the current, which was small in the arc light, was very large in the case of the spark discharges used, and therefore the movement of the spark in the latter case was practically determined by the heating effect in consequence of the relatively small importance of the electro-magnetic effect.

Prof. S. P. THOMPSON remarked that similar effects could be produced by an alternating current working an ordinary induction-coil.

The Society then adjourned until November 10th, when the meeting will be held in the Central Technical Institute.

NOTICES OF BOOKS.

Index to the Literature of Thallium, 1861—1896. By Martha Doan. Smithsonian Miscellaneous Collections, No. 1171. Washington City, 1899. Pp. 26. 8vo.

This contribution to chemical bibliography bears the endorsement of the Committee on Indexing Chemical Literature appointed in 1882 by the American Association for the Advancement of Science. It presents in chronological order the most important references to papers on thallium and its compounds found in a large number of periodicals. This compilation is the first of the series that bears the name of a woman. Miss Doan was a student at Cornell University, in New York State.

An author-index completes the work.

School Chemistry. By Charles Baskerville, the University of North Carolina. Richmond, Va.: B. F. Johnson Publishing Co. 1899. Pp. 159. 12mo.

This elementary work is the outcome of five years' experience in teaching teachers in the summer school of the University of North Carolina. The course is planned to cover forty weeks when one hour per week is devoted to it; of this hour, only thirty minutes is given to the performance of experiments, fifteen being given to reading aloud by the pupils the daily lesson, and fifteen to questioning them on the preceding lesson. The book is notable for the very large number of topics briefly treated.

A few slips may be corrected in a second edition: the "lunar caustic" used as a cautery is not crystalline, but fused silver nitrate. The simple experiments seem to be well chosen, and all the apparatus needed for ten pupils to carry them out can be bought in New York for 25 dollars.

Descriptive Chemistry. A Text-book for Short Course. By S. E. Tillman. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1899. Pp. x.—429. 8vo. Ill.

Colonel Samuel E. Tillman, U.S. Army, has been for many years giving instruction in chemistry, mineralogy, and geology to the cadets at the U.S. Military Academy, West Point, N.Y. The time allowed for chemistry by the Faculty is only two months, or about two hundred hours for instruction, study, and other work on the subject, and the Professor is of the opinion that, under these limitations, "the unique disciplinary training for which chemistry is so admirably adapted as a laboratory science can only be very imperfectly attained." And therefore he is obliged to make the acquisition of knowledge the essential feature in the curriculum; this is secured by careful study of the proper text, well-conducted recitations, and explanatory lectures illustrated with experiments. Hence this text-book, which "aims to give a concise statement of the more fundamental principles of chemistry, together with that class of chemical information most essential to cultured men." The first chapter contains the principles of chemistry in language not too difficult to be grasped by fairly equipped students. The second chapter discusses the causes influencing chemical processes, and a statement of the Periodic Law; then follow chapters on the non-metals and metals. About one-fourth of the book is taken up with organic chemistry and the applications of chemistry. Under the latter heading there are sections on glass-making, pottery, explosives, coal-gas, beer, wine, distilled liquors, bread, soap, leather, cheese, and dyeing. Throughout the handsomely printed volume two sizes of type are used; the smaller for less important matter. The illustrations are from original drawings made by Colonel Tillman's assistants.

The West Point Professor has produced an admirable book, written in clear, forceful style. The arrangement is one that appeals to common sense, and the selection of material is made with judgment. The author is conservative, and introduces no impracticable novelties. The book ought to find a wider field than the embryo army officers, especially as it has little distinctively military. To one word the reviewer takes exception—"stochiometry" as a substitute for the correct form stoichiometry (*stoicheion*).

Teachers having no fads will welcome this excellent book.

Indicators and Test-papers: their Source, Preparation, Application, and Tests for Sensitiveness. A *résumé* of the current Facts regarding the Action and Application of the Indicators and Test-papers which have been proposed from time to time and are in Present Use in Chemical Manipulations. With a Tabular Summary of the Application of Indicators, designed for the Use of Chemists, Pharmacists, and Students. By Alfred I. Cohn. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1899. Pp. x.—249. 12mo.

This volume has so many words on the title-page that it leaves little for the reviewer to do besides making the statement that the author has carried out his programme very carefully. He gives the source, preparation, properties, tests, and application of seventy-six indicators and seventy-four test-papers, arranged alphabetically in two divisions. In compiling the book the author has examined chemical journals and reports of societies in five languages.

Chemists employing volumetric methods will find this a useful book for reference.

H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 8.

Some Criticisms on M. Raoult's Cryoscopic Measurements.—A. Ponsot.—A controversial paper, not suitable for abstraction.

Method of Determining Molecular Weights, based on the Measurement of the Tension of Dissociation of the Hydrates of Gases.—G. Rosset.—Instead of measuring vapour-tensions, always very small in the case of aqueous solutions, the author endeavours to deduce them from the measurements of the tensions of dissociation of gaseous hydrates; these being much greater, enable measurements of relatively greater precision to be made. At 0°, for example, the dissociation tension of hydrate of chlorine varies 40 m.m. for a change of 0·1 m.m. in the vapour-tension of the aqueous solution, on contact with which it is dissociated. The method in question consists of measuring the dissociation-tension of a suitable gaseous hydrate in contact with an aqueous solution containing a known weight of a substance of which we wish to find the molecular weight, and to imitate this tension with the corresponding tension in the presence of pure water.

On Glycerophosphoric Acid.—J. Cavalier and M. Pouget.—According to Pelouze, the alkaline-earthy

glycerophosphates are less soluble hot than cold. The authors have measured the solubility of glycerophosphate of lime in water at different temperatures, and obtained the following results:—

100 grms. of solution contained at—	Anhydrous glycerophosphate of lime.
16°	7·9 grms.
36°	4·4 ,,
51°	2·3 ,,
77°	1·3 ,,
86°	1·25 ,,
100°	1·15 ,,

Consequently, a cold saturated solution deposits the greater part of its salt on boiling, retaining only one-eighth part. Glycerophosphate of barium behaves in a somewhat different manner; its solutions being more easily decomposed by heat, and the precipitation by heat is less abundant. The authors have also estimated the speed of decomposition of glycerophosphoric acid by water at a temperature of 88°, and they found that it has less stability than the ethylic compound, but about the same as the methylic and allylic ethers.

Action of the Hydrazines on the Chloranilic and Bromanilic Acids.—A. Descomps.—The author has already announced the preparation of a compound which takes place when one molecule of chloranilic acid, dissolved in alcohol at 80°, is treated with two molecules of phenylhydrazine. Continuing his research, he has acted with phenylhydrazine on bromanilic acid under the same conditions. A voluminous pale red precipitate is immediately formed answering to the formula $C_6O_2Br_2 < \begin{matrix} OH—C_6H_5NH—NH_2 \\ OH—C_6H_5NH—NH_2 \end{matrix}$. This compound, designated by the letter α, is susceptible, like the α-derivative of chloranilic acid, of being transformed under the influence of alcohol at 90° into an isomerous β-derivative, crystallised in prisms of an intense violet-brown colour; but the transformation, which was complete with the chloranilic acid derivative, is in this case only partial.

MISCELLANEOUS

The Paris Exhibition.—Mr. C. Wilkes, 29, Ludgate Hill, London, has been appointed General Manager and Sole Agent for the British Empire (Canada excepted) for all English advertisements or publicity in the General Official Catalogue of the Paris 1900 Universal Exhibition; also for the French and English Guides and other publications issued by Messrs. Lemercier and Co., Official Contractors to the French Government and Exhibition Board.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"Nitragin" and Soil Ferments.—I should feel much obliged if any of your correspondents will inform me of any publications, books or pamphlets, or Society's papers or lectures, which touch at all upon (1) soil ferments, (2) "nitragin," which may have appeared during the last three years, or anything connected with microscopic life (late advances) in the soil.—HOWARD B. EVANS.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "On 'Velvril' Material, a new Substitute for India-rubber and Gutta-percha," by Walter F. Reid, F.I.C., F.C.S.
WEDNESDAY, 8th.—Geological.
FRIDAY, 27th.—Physical, 5. (At Central Technical College, South Kensington). "Contact Electricity," by F. S. Spiers. "Heat of Formation of Alloys," by J. B. Tayler.

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October, 1899.

THE CHEMICAL NEWS.

Vol. LXXX., No. 2085.

THE PRESENCE OF POTASSIUM NITRITE IN BROWN POWDER RESIDUE WHEN THE POWDER IS BURNT IN AIR UNDER ORDINARY PRESSURE.

By Lieut. SETON, R.A., and Lieut. STEVENSON, R.A.

Ordinary black powders when burnt in air under ordinary pressure leave a small quantity of residue in which carbonate, sulphate, and sulphide of potassium predominate. Traces only of nitrate and nitrite and other components can usually be found. When examined quantitatively, however, the three salts above mentioned together make up some 98 per cent of the whole. Brown powders burn much more slowly, and in consequence the residue is larger. It is generally white or greyish-white, hygroscopic, and for the most part soluble in water.

Some analyses were made of these brown powder residues to determine the relation of sulphate to carbonate. No sulphide is as a rule present. It was first noticed on acidifying that red fumes were produced. This of course indicated presence of nitrites in more than mere traces.

Several determinations of the amount of nitrite, by permanganate and by the nitrometer, gave about 6 per cent calculated as KNO_2.

The figures of one complete analysis of residue from a brown powder are :—

K_2CO_3	61·96
K_2SO_4	26·18
KNO_2	6·17
Silica and other substances insoluble in H_2O..	5·8
	100·11

Ordnance College, Woolwich.

ON THE SOLUTION OF AN IRON ANODE IN A SOLUTION OF ACETATE OF SODIUM AND ACETIC ACID.

By G. ARTH.

It has been well known since Renault's experiments on batteries (*Ann. Chim. Phys.*, 1867, vol. ii., p. 137) that an iron electrode dissolving in the circuit formed on itself always dissolves in the bivalent state whatever the electrolyte used may be, even when composed of oxidising liquids, such as a solution of chlorate of potash containing hydrochloric acid, or even dilute aqua regia. Round the anode there forms a blue zone if a drop of ferricyanide of potassium be carefully added, which indicates the presence of a ferrous salt; this reaction cannot, however, be obtained beyond a certain distance from the electrode on account of the oxidising action of the solution used.

It appears that this reaction does not always take place —at least, not under special conditions, and when the iron anode is submitted to the action of a current produced outside the cell in which it is dissolved. The following is the arrangement adopted for the experiments, which gave different results :—

A strip of iron, as pure as possible, 50 m.m. long by 12 to 15 m.m. wide and about 2 m.m. thick, was suspended by a platinum wire in the centre of a platinum cylinder of the same height and about 35 m.m. diameter. The whole was plunged in a jar of 15 c.m. high, filled with a solution of acetate of sodium containing acetic acid (generally 50 grms. of crystallised acetate and 50 grms. of glacial acid per litre). The strip of iron is connected with the positive pole and the platinum cylinder with the negative pole of an accumulator battery. An ammeter and a rheostat must be placed in circuit, and a voltmeter connected to the terminals of the cell.

a. In this solution the strip of iron only dissolves, naturally, to a very slight extent; but as soon as the circuit is closed, even when only a very small current at a low voltage is passed, the solution of the iron commences at once. The salt produced forms colourless striæ, which are easily seen below the strip of iron, and the disengagement of gas is hardly perceptible at the surface of the metal, while bubbles of hydrogen appear immediately on the platinum cylinder. The phenomenon remains thus so long as the current does not exceed certain limits. It is easy to make certain that during this period the iron dissolves in the bivalent state, as in Renault's experiments, and that only ferrous acetate is formed. The liquid, in fact, remains colourless, the yellow prussiate does not give any Prussian blue, and if a silver voltmeter is placed in the circuit we find the atomic relation $\frac{\frac{1}{2}\,Fe}{Ag} = \frac{28}{107·93}$ almost theoretically correct between the weight of silver deposited and the weight of iron dissolved.

No.	Volts.	Ampères.	Fe dissolved.	Ag deposited.	Time. h. m.	Relation.
I.	0·79—0·92	0·17—0·10	0·2275	0·8645	2 —	$\frac{28·40}{107·93}$
II.	1·05—1·35	0·36—0·25	0·4894	1·8736	1 45	$\frac{28·19}{107·93}$

b. If the current traversing the cell is more intense, the phenomenon is quite different. I have observed two cases which it is necessary to mention. At a certain moment the strip of iron became polarised, the needle of the voltmeter goes up while that of the ammeter goes down; the iron generally becomes covered with a reddish zone of liquid, which disappears after a few moments, at the same time that gas comes off abundantly from the surface of the metal. In this case the iron strip may become almost passive (especially if it is polished), as the results of the two following experiments show :—

No.	Volts.	Ampères.	Fe dissolved.	Ag deposited.	Time. h. m.	Relation.
I.	2·93—3·50	0·31—0·38	0·023	1·080	— 50	$\frac{2·29}{107·93}$
II.	3·20—3·36	0·34—0·41	0·0195	1·6725	1 10	$\frac{1·25}{107·93}$

The small amount of iron dissolved is always found in the ferric state.

c. In other experiments, after the polarisation of the iron, a very small quantity of gas only is given off at the surface of the iron, and the sharp red striæ are seen below, caused by the formation of ferric acetate; the colour of the liquid and the reaction with ferrocyanide of potassium indicate the formation of a salt with the maximum quantity of iron. If we now place a silver voltmeter in the circuit we obtain the following results :—

No.	Volts.	Ampères.	Fe dissolved.	Ag deposited.	Time. h. m.	Relation.
I.	2·24—2·41	0·11—0·05	0·0844	0·4532	2 15	$\frac{20·09}{107·93}$
II.	2·70—2·80	0·2	0·5618	3·1547	4 20	$\frac{19·21}{107·93}$
III.	2·80—3·07	0·24—0·19	0·3907	2·0016	2 45	$\frac{21·06}{107·93}$
IV.	3·20—3·30	0·42—0·28	0·1693	0·9505	— 50	$\frac{19·22}{107·93}$
V.	3·53—3·60	0·41—0·32	0·4586	2·5910	2 5	$\frac{19·10}{107·93}$

Theoretically, the relation is $\frac{\frac{1}{3}\,Fe}{Ag} = \frac{18{\cdot}66}{107{\cdot}93}$. In spite of the disengagement of a small quantity of gas, the figures obtained in these experiments are always a little higher than the theoretical value 18·66; a certain portion of the iron must therefore be dissolved in the bivalent state, and, as a matter of fact, ferricyanide of potassium always gives a blue precipitate in the liquid close to the iron. However this may be, the relations found seem to prove that ferric acetate is formed directly by the solution of the iron in the trivalent state, and not by the subsequent oxidation of the ferrous acetate first formed. Further, one can see no reason why ferrous acetate should be oxidised in this series of experiments, as in the first series it is not oxidised in an identical solution.

With regard to these phenomena, we must not forget the experiments and the theory of Wohlwill on the ions of tri- and mono-valent gold (*Zeit. fur Elektrochemie*, iv., pp. 379, 402, 421). I have not yet been able to determine exactly how and at what moment these changes take place. The phenomenon appears to be very complex, and depends on a considerable number of factors. I propose, however, to continue the research, using solutions of varied composition.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 16.

COMMERCIAL SEPARATION OF COPPER FROM THE ELECTRO-POSITIVE GROUP OF METALS (NICKEL, COBALT, IRON, ZINC).

By B. NEUMANN.

In the electrolytic refining of copper a certain number of metals contained in the anode (raw copper) pass directly into the slimes. These are:—Silver, gold, platinum, bismuth, tin, arsenic, antimony, and lead. Other metals are not precipitated from the solution, except by prolonged standing after saturation. The most electro-positive metals (nickel, cobalt, iron, and zinc) are dissolved from the anode at the same time as the copper, but are not deposited at the cathode on account of the low electromotive force used. The bath, which is originally formed of an acid solution of sulphate of copper, thus gradually becomes enriched with metals of this group, and at the same time becomes poorer in copper. If the anode contains a much higher proportion of electro-positive metals than is generally found in raw copper, such as is the case with brass, old cartridge cases, German silver, &c., pure copper will still be deposited at the cathode so long as the electro-motive force used is not higher than that generally used in refining copper.

The problem the author has studied is the examination of the character of the electrolytic copper deposited at the cathode when working with baths charged more or less with electro-positive metals. The conclusions arrived at may be summed up in the following manner:—

Alloys of copper with the electro-positive metals, such as nickel, cobalt, iron, and zinc, can be refined in the ordinary manner. Copper alone is deposited at the cathode, the other metals remaining in solution. The electromotive force should not exceed 0·5 volt for each bath. As the electrolysis progresses the resistance of the electrolyte increases on account of its loss of copper, and gains in foreign metals; the effective return from the current thus diminishes. Further, the quality of the copper deposited becomes less and less satisfactory, so that at a certain moment it becomes necessary to stop the operation.

The experiment of Fœrster and Seidel has shown that the precipitation of the reddish brown pulverulent copper is caused by the occurrence of a certain concentration of the solution too weak in ions of copper. In the refining of alloys of copper, therefore, a point is at last reached where only spongy copper is deposited. The addition of sulphuric acid in no way remedies this inconvenience, and, according to the law of the action of masses, such an addition would even tend to favour the formation of spongy copper. The only practicable method is therefore to withdraw the liquor and precipitate the copper from it by means of sulphuretted hydrogen, and to proceed with the electrolysis in a fresh sulphuric bath. The use of sulphuretted hydrogen to precipitate the rest of the copper is, further, more economical than the introduction of anodes, either insoluble or composed of electro-positive metals.

An Austrian company is at present refining raw copper containing 20 per cent of impurities. Under these conditions Canadian ores, which contain equal parts of copper and nickel, might easily become of much greater value than they now possess, owing to the difficulty of their treatment.—*Zeitschr. fur Elektrochemie*, vol. iv., pp. 316—322, and 333—338.

ON THE CAUSES OF EXPLOSION IN THE MANUFACTURE OF BRONZE POWDERS.

By M. STOCKMEIER.

Several explosions have been recorded in the last few years in factories where aluminium-bronze powder is ground. The author has made several experiments with a view to ascertaining under what conditions explosions are possible.

He has found that the powder itself is stable both to shock and while being ground. When mixed with chlorate of potash it detonates either when struck or by simply rubbing. It can also be detonated by means of an electric spark when shaken up in a vessel containing air. Aluminium-bronze is capable of decomposing water; the quantity of hydrogen produced varies under certain conditions, such as the nature and quantity of the grease always present. The bronze powder is hygroscopic, and, according to the author's experiments, it is capable, when dry, of absorbing up to 1·40 per cent of atmospheric moisture. Thus, in grinding up 5 or 6 kilogrms. of bronze powder, at 1·4 per cent of water, we can produce 43·4 to 52·08 litres of hydrogen. This hydrogen forms with air a detonating mixture which may be exploded by a spark produced by the passage of a small stone or other foreign body through the rollers.

The most effective method of preventing these explosions would be to replace the air which comes in contact with the powder by an inert gas, but unfortunately such a thing is quite impracticable.

All risk of explosions may, however, be avoided by observing the following precautions:—

1. The powder must be perfectly dry before being placed in the grinding machine.

2. The shop in which the grinding is carried on should be as nearly as possible kept at the same temperature as the machines in operation.

3. If the powder becomes brown during the grinding the machine must be stopped, the charge removed and placed in a cool place, and the machine carefully cleaned and aired.

4. The shop should also be well aired if the powder begins to show signs of attack during drying, or while being mixed in the receivers.

5. The Quirn-Schmidt apparatus should not be used, as it is not sufficiently safe.

6. The finished powder should not be packed in the grinding shop.

7. The grinding machines should be frequently examined.

8. The air should be kept as free as possible from aluminium dust.—*Zeits. f. Untersuch. Nahr. u. Genuss-mittel*, 1899, p. 49.

AQUEOUS SOLUTIONS OF METALLIC GOLD.

By R. ZSIGMONDY.

THE author gives a few details for the preparation of a red solution of *colloidal gold*. The following method gives good results:—25 c.c. of a solution of chloride of gold (hydrochlorate of chloride of gold) containing 0·6 grm. per litre, are diluted with 100—150 c.c. of distilled water, and 2 to 4 c.c. of a double decinormal solution (0·2 N) of carbonate or bicarbonate of potassium. The slightly alkaline solution thus obtained is boiled, the flame is then withdrawn, and 4 c.c. of a solution containing one part of recently distilled formic aldehyde (boiling-point 97—100°) in 100 parts of water, are carefully but rapidly added, the solution being continuously stirred all the while. The reaction is over in a few seconds, and the solution, colourless at first, takes a very brilliant red tint.

The success of the operation appears to depend on the purity of the distilled water used. Mere traces of phosphate will prevent the reaction. Very often the solution obtained has a violet or blue-black colour, and is not clear. It is impossible to prepare large quantities (2 or 3 litres) of the red solution at one time, on account of the difficulty experienced in adding the formic aldehyde sufficiently quickly.

Solutions prepared as described above, and containing 0·005 per cent of gold, can be boiled, or kept for several months without undergoing the slightest change. On submitting the solution to dialysis in a warm place (40—50°), foreign matters can be eliminated, and the proportion of gold present be brought up to 0·12 per cent.

The author then describes the properties of the solution of colloidal gold: he arrives at the conclusion that the gold is really dissolved in the water, and is not in the state of particles of metallic gold or oxide of gold in suspension in the liquid. Most acids and mineral salts re-precipitate the gold from this solution.

In 1857 Faraday prepared similar coloured liquids; but he expressed the opinion that the gold existed in the state of extremely finely divided metallic particles.

The author is examining the relationship existing between these auriferous liquids which he has prepared and purple of Cassius.—*Annalen*, cccl., [1], p. 29.

ON THE PURIFICATION OF IRIDIUM.

By E. LEIDIE.

WHEN we purify commercial iridium by Sainte-Claire Deville and Debray's method (fusion of the metal with lead, and subsequently attacking the ingot with nitric acid and aqua regia), we obtain a residue which should contain only iridium, ruthenium, and a little iron; but if the proportion of rhodium to be removed is too great, if the iridium is obtained from osmides not quite free from osmium, and if the attack of the metal by lead and that of the ingot by the acids has been incomplete, then the residue further contains rhodium, osmium, lead, and sometimes gold.

The originators of the method have mentioned these facts, and have further described a method which enables us to separate the foreign metals from iridium, but their process necessitates the use of a series of long and delicate operations.

The following method, which is specially applicable to the separation of the above-mentioned metals from iridium, is based on their transformation into chlorides, and on the systematic use of nitrite of sodium; the following is a *resumé* of the method:—

I. The iridium, finely powdered and mixed with double its weight of melted chloride of sodium, is heated in a current of dry chlorine at a dull red heat; all the metals are thus transformed either into chlorides or double chlorides. The cooled mass is treated with about twenty-five or thirty times the weight of metal used, of water slightly acidulated with hydrochloric acid; it is then filtered; all the metals are in solution in the state of chlorides.

II. This solution is heated to about 50—60°, and small quantities of nitrite of sodium are progressively added until nitrous fumes are no longer given off and it has become neutral to litmus. Carbonate of sodium is then added until the solution is distinctly alkaline, when a fresh quantity of nitrite of sodium is added; this must be done very carefully, on account of the disengagement of gas if osmium is present; it is then boiled for a few moments and filtered. Under the influence exercised by nitrite of sodium under these conditions, that is to say, in a medium first neutral and then alkaline, the iron and lead in the form of oxides, and the gold in the metallic state, have been precipitated and remain on the filter; the chloride of osmium is transformed into osmiate of sodium, OsO_4Na_2, and the chlorides of ruthenium, rhodium, and iridium into the corresponding double nitrites, $Ru_2(NO_2)_4,4NO_2Na$, $Rh_2(NO_2)_6,6NO_2Na$, and $Ir_2(NO_2)_6,NO_2Na$,—all four soluble in water.

III. To this solution an excess of soda is added, and a current of chlorine is passed through, first in the cold, and afterwards while heating gradually up to 50—60°; the alkaline hypochlorite formed causes the osmium and ruthenium to pass to the state of peroxide of osmium, OsO_4, and peroxide of ruthenium, RuO_4, which distil under the influence of heat; care must be taken that the apparatus used for distillation should be formed entirely of glass. These peroxides are collected first in a tube plunged in ice, and then in a flask containing potash.

IV. The solution contains only nitrites of rhodium and iridium, with the alkaline chlorate and nitrate formed during the course of the operation. By acidulating this solution with hydrochloric acid, evaporating to dryness, and once more repeating the reaction with acid and evaporating, a saline residue may be obtained containing only chloride of sodium, with the double chloride of rhodium, $Rh_2Cl_6,6NaCl$, and the chloroiridiate, $IrCl_4,2NaCl$; this residue is taken up with cold chlorine-water, the solution is set to crystallise so as to separate the greater part of the chloride of sodium which is first deposited. The crystals which form last are a mixture of the two above-mentioned chlorides, $Rh_2Cl_6,6NaCl$ and $IrCl_4,2NaCl$. These crystals are drained and thoroughly dried at 105°, after which they are heated for four hours at 440° (in a sulphur vapour oven) in an apparatus traversed by a current of dry chlorine; the mass is allowed to cool in a current of chlorine and then treated with cold chlorine-water. The double chloride of rhodium is transformed into a mixture of chloride of sodium soluble in water, and insoluble sesquichloride, Rh_2Cl_6, like that prepared at a high temperature in the dry way; as to the chloroiridiate it remains unchanged, the Rh_2Cl_6 is separated by filtration.

V. The filtrate contains only chloride of sodium and chloroiridiate of sodium; the latter, by the addition of a large excess of chloride of ammonium, is precipitated in the form of chloroiridiate, $IrCl_4,2NH_4Cl$, insoluble in a saturated solution of sal-ammoniac; it is thrown on a filter, and washed with a saturated solution of sal-ammoniac to remove all the chloride of sodium. There now only remains to dry the chloroiridiate of ammonium, and to decompose it by heating to dull red in a current of hydrogen, and allowing it to cool in a current of dry carbonic acid. Thus we obtain pure iridium.

To succeed in the separation of rhodium from iridium

it is necessary to observe two indispensable precautions: *a*. An excess of chloride of sodium should be guarded against; this substance, in fact, gives stability to the double chloride, $Rh_2Cl_6,6NaCl$, which can be maintained in an unaltered state in a mass of melted chloride of sodium; the rhodium salt should therefore be dissolved with that of iridium.

b. The chlorine must be perfectly dry; in fact, at 440° in the presence of water vapour it gives rise to the formation of hydrochloric acid, and the chloroiridiate heated in this gas at 440° decomposes into chlorine and sesquichloride, Ir_2Cl_6, of which a part would pass into solution with the rest of the iridium in the form of the double chloride, $Ir_2Cl_6,6NaCl$, but the other part of which would remain with the rhodium in the form of the sesquichloride, Ir_2Cl_6, insoluble in water.

This method, the application of which to a particular case I have just described, may be generalised.

I propose shortly to publish its application to the general case of the separation of the metals of the platinum group, one from the other, by the wet method.—*Journ. de Pharm. et de Chim.*, Series 6, vol. x., No. 4.

ON A CHLORO-IODIDE OF TIN.

By C. LENORMAND.

In a previous paper (*Journ. de Pharm.*, 13 Sept., 1898), I described the conditions under which a new compound, $SnCl_2I_2$, is produced. I also showed that when distilled in air it left a residue of SnI_4, and gave as distillate a liquor in which tin was found, as well as chlorine and iodine, in undefined proportions, but which contained all the chlorine contained in the original product. I showed that this liquor, when distilled several times, allowed a quantity of iodine decreasing successively to pass, and at the fifth distillation in air, nothing but bichloride of tin passed over. I then showed that the final decomposition of $SnCl_2I_2$ ought to take place according to the following formula, $2(SnCl_2I_2) = SnCl_4 + SnI_4$.

At the end of the paper I remarked:—"The decomposition of $SnCl_2I_2$ takes place according to the preceding formula; but according to what formula do the first and succeeding distillations take place? Stannic iodide forms the residue at each distillation; now this body is not volatile at the temperatures at which I worked; how therefore does the iodine pass over on distillation? Must we admit the formation of an intermediate volatile chloro-iodide of tin?"

Since then I have taken up this subject again; but instead of carrying on the distillation in the ordinary manner, I did it in a fractional distillation apparatus; at 126° a red coloured liquid came over, then the temperature gradually rose until it reached 180°, where it appeared to stop. But on prolonging the heating it finally reached 280°, where it stopped definitely; at precisely this moment a phenomenon occurred which I had never noticed before on account of the form of my first apparatus; the escape tube became filled with an orange-red crystalline product. On analysis this body showed the composition of a chloro-iodide, $SnClI_3$

The liquid distilled between 126° and 180°, rectified, not in air this time, but in vacuo, allows another liquid to pass between 28° and 30°, the composition of which shows it to be stannic chloride, and leaves a residue the composition of which varies with the duration of the rectification. In fact, if this be stopped when the distillate is about two-thirds of the original volume, the residue has the formula of a chloro-iodide, $SnCl_3I$; if, on the contrary, instead of stopping the distillation at this moment, it is allowed to go on longer, the composition of the residue is that of a chloro-iodide of tin, $SnCl_2I_2$.

According to these observations, the decomposition, by heat, of the chloro-iodide, $SnCl_2I_2$, takes place according to the following formula—

$$5SnCl_2I_2 = SnCl_4 + SnCl_3I + SnCl_2I_2 + SnClI_3 + SnI_4.$$

The liquid distilled in air thus consists of (1) stannic chloride; (2) the chloro-iodide, $SnCl_3I$; (3) part of the original chloro-iodide, $SnCl_2I_2$; (4) the chloro-iodide of tin, $SnClI_3$.

The chloro-iodide of tin, $SnCl_2I_2$, distilled direct in vacuo, behaves in a much more simple manner; there are no intermediate compounds formed, but we at once obtain, under a pressure of a few m.m.:—

1. Stannic chloride which distils over;
2. Stannic iodide which remains as the residue.

The direct decomposition of this compound in vacuo is therefore represented by the formula—

$$2SnCl_2I_2 = SnCl_4 + SnI_4.$$

On a Bromo-iodide of Tin.—Iodide in the cold is without action on protobromide of tin, but when we use, as I did, a closed vessel at 100°, an energetic reaction takes place; the mass becomes liquid and the iodine disappears in the proportion of 254 grms. of this body for 278 grms. of protobromide of tin.

The new compound, liquid at 100°, is not so at the ordinary temperature; it is then solid and occurs as a crystallised reddish-orange mass.

After careful decantation at 100° it gave on analysis the following results:—

	Calculated. $SnBr_2I_2$.	Found.		
Tin	22·18	22·38	22·31	22·23
Bromine ..	30·08	29·56	29·62	29·60
Iodine ..	47·74	47·19	47·54	47·68
	100·00	99·13	99·47	99·51

Its composition therefore corresponds to that of a bromo-iodide of tin, $SnBr_2I_2$.

I estimated the bromine and iodine by Rose's method, and the tin by the method I have previously described.

This new compound is solid at the ordinary temperature, it is orange-red in colour, and crystallises in hexagonal tables. At 50° it commences to melt, when liquid it has a beautiful ruby colour. In this state it gives off very little fumes, and when cold none at all. Its density taken at 15° equals 3·631. When placed in water it is difficultly soluble in the cold; on raising the temperature it dissolves rapidly. Towards 80° its aqueous solution decomposes into insoluble hydrate of oxide of tin, and into hydrobromic and hydriodic acids which remain dissolved.

When submitted to the action of heat in a fractional distillation apparatus, it begins to melt at 50°, and boils at 225°.

Between 230° and 250° a product is distilled over which crystallises in orange-yellow crystals in the escape tube; the formula of this body is that of a bromo-iodide, $SnBr_3I$.

Between 250° and 275° a product is collected which again crystallises in the escape tube; its composition is that of the original bromo-iodide, $SnBr_2I_2$.

Finally, at this moment there remains in the flask an orange-red compound, having the composition of the bromo-iodide, $SnBrI_3$.

According to these observations the decomposition in air of the bromo-iodide, $SnBr_2I_2$, may be represented by the formula $3SnBr_2I_2 = SnBr_3I + SnBr_2I_2 + SnBrI_3$.

When distilled in vacuo the bromo-iodide, $SnBr_2I_2$, boils at 130°, and distils a little above this point; the temperature increases gradually and reaches 180°, at which point it remains. At this moment the product distilled has the composition of a bromo-iodide, $SnBr_3I$, and the residue that of another bromo-iodide, $SnBrI_3$.

Thus the decomposition in vacuo of the bromo-iodide, $SnBr_2I_2$, is not effected like that of the chloro-iodide

$SnCl_2I_2$, since the formula which expresses its decomposition is the following, $2SnBrI_2 = SnBr_3I + SnBrI_3$.—*Journ. de Pharm. et de Chim.*, Series 6, vol. x., No. 3.

ELECTROMOTIVE PROPERTIES OF CHROMIUM: ACTIVE AND PASSIVE CHROMIUM.

By W. HITTORF.

In a paper presented to the German Electro-chemical Society, the author describes the results of some experiments made with two samples of metallic chromium prepared according to Goldschmidt's process.

According to Wöhler zinc precipitates metallic chromium from its melted salts; we might therefore conclude that chromium would immediately follow zinc at the positive end of the electromotive series of metals. It has, however, been found that when chromium is plunged into certain solutions, such as dilute hydrochloric acid, which do not cause a disengagement of hydrogen at the ordinary temperature, not only is it electro-negative with regard to zinc, but also to cadmium, iron, nickel, copper, mercury, and silver. It is without action on the neutral salts of these metals even when boiling. The chlorides of gold, palladium, and platinum are also unattacked. Only the bichlorides of mercury and copper and cupric bromide are reduced to the state of mercurous and cuprous salts at boiling point. From this point of view chromium behaves therefore like silver; but at a low temperature it behaves generally like a noble metal.

It must be remarked that chromium forms three kinds of compounds corresponding to the three degrees of oxidation, CrO, Cr_2O_3, CrO_3, and that when we use it as an anode for the electrolysis of a single electrolyte, $ZnCl_2$, it dissolves, forming different compounds according to the temperature, and according to the nature of the solvent used.

Chromium exists in three distinct states, *passive*, *active*, and *indifferent*; under each of these forms it occupies a different position in the electromotive series of metals, and possesses different chemical properties.

In the *passive* state it is a noble metal. It has no reducing action on the salts of other metals, and follows platinum at the end (electro-negative) of the electromotive series of metals. This is its normal condition at the ordinary temperature, and when it is used as an anode in the electrolysis of chloride of zinc, chloride of sodium, hydrochloric acid, &c., it dissolves, forming chromic acid, which colours the solution in the neighbourhood of the anode yellow.

In the *active* state, which is generally manifest at higher temperatures, it immediately follows zinc in the voltaic series, and displaces all the more electro-negative metals from their solutions.

Used as an anode in the electrolysis of the chlorides at boiling point, it dissolves in the state of protochloride, $CrCl_2$, colouring the solution a bluish green. In certain cases it is necessary to heat the solution to above 100°, as, for example, when we electrolyse the chlorides of magnesium or zinc. An anode of chromium remains passive in a dilute boiling solution of chloride of zinc containing an excess of oxide of zinc to neutralise all trace of hydrochloric acid, and we notice the yellow colouration of chromic acid. If, on the contrary, the solution is slowly evaporated the temperature rises gradually to about 130° on account of the concentration, and at this temperature we notice the green colour due to protochloride of chromium, $CrCl_2$. The passage of chromium from the inactive or passive state to the active state is again placed in evidence by the following experiment.

Passive chromium can be kept for no matter how long a time in solutions of chloride of copper, gold, palladium, or platinum without reducing them. But if we place it in a boiling solution of chloride of potassium or sodium it immediately passes to the active state. Consequently, a fragment of chromium which, being used as an anode, has given chromic acid by electrolysis can be kept as long as is wished in a boiling solution of a chloride of a noble metal without there being a trace of reduction. But if we add an alkaline chloride reduction immediately takes place. This action is the more feeble as the quantity of alkaline chloride added is itself small. Further, it only takes place at a high temperature, and ceases as soon as the solution is allowed to become cold.

In the *intermediate* or *indifferent* state chromium occupies an intermediate position in the electromotive series and forms a compound which is also intermediate. The electrolysis of an alcoholic solution of chloride of zinc furnishes a green solution of $CrCl_3$ at the point of contact with the chromium anode.

Passive chromium does not combine with iodine, even in the nascent state, while the active modifications displace the iodine from hydriodic acid.

The author has also studied the action of chromium on the melted metallic salts. He admits that the passive state of iron can be explained by the formation of an invisible layer of oxide which protects the metal against any outside attack, but a similar explanation cannot be admitted in the case of chromium, as experiments have shown that such is not the case.

Finally, up to the present, no acceptable theory has been offered concerning these curious properties of chromium. In its several states this metal possesses properties so different, that one is almost tempted to attribute them to distinct metals rather than to one only.—*Zeitschr. fur Elektrochemic*, 1898, iv. [21], p. 481.

PHOTO-CRYSTALLISATION.*

By FERDINAND G. WIECHMANN, Ph.D.

(Continued from p. 217).

Inspection of Table IV., which is self-explanatory, shows the following effects of exposure to light. All specimens in Series I. (exposed to direct sunlight) which crystallised completely, had attained to complete crystallisation long before any specimen in either of the other two series had reached this condition.

Thus, between the times of complete crystallisation of No. 1, Series I., and No. 10, Series II., the first of Series II. to crystallise wholly, there elapsed 484 days. Between the complete crystallisation of No. 1, Series I., and No. 14, Series III., the first of this series to crystallise completely, lies a period of 964 days.

All three series of specimens were kept in the same room throughout the entire time over which observation extended. Series II. and III. were therefore practically under identical temperature conditions. Series I., however, being exposed to direct sunlight undoubtedly received more heat-energy than the other series. Experiments in which this disturbing factor will be eliminated, by filtering the sunlight through a concentrated solution of alum before it reaches the sucrose solutions, are contemplated.

From these data it appears that, *cæteris paribus*, photo-crystallisation is directly proportionate to the intensity of illumination.

Nine specimens when taken for analysis were wholly crystallised. This is 50 per cent of the total number. These had turned solid in the following sequence and time (see Table V.).

In Series I. five out of the six specimens had crystallised completely, and it will be of interest to learn what relation the sequence of crystallisation bears to the composition of the specimens and the conditions to which they were subjected.

* *School of Mines Quarterly*, vol. xvii., No. 4.

TABLE IV.

Number of sample.	Description of sample. Per cent invert.	Description of sample. Condition.	Condition of exposure.	Time, in days from beginning of experiment to— Appearance of first crystal.	Complete crystallisation.	Analysis.	Condition when analysed.
1.	90·9	Acid	Direct sunlight	25	127	273	Solid.
2.	90·9	Neutral	,, ,,	25	281	333	,,
3.	80·6	Acid	,, ,,	25	225	273	,,
4.	80·6	Neutral	,, ,,	25	324	333	,,
5.	58·0	Acid	,, ,,	63	350	488	,,
6.	58·0	Neutral	,, ,,	99	—	1474	Semi solid.
7.	90·9	Acid	Diffuse daylight	25	1096	1114	Solid.
8.	90·9	Neutral	,, ,,	25	—	859	Very nearly solid.
9.	80·6	Acid	,, ,,	—	—	1475	Nine-tenths solid.
10.	80·6	Neutral	,, ,,	—	611	810	Solid.
11.	58·0	Acid	,, ,,	—	692	810	,,
12.	58·0	Neutral	,, ,,	170	—	1476	Semi-solid.
13.	90·9	Acid	Darkness	25	—	1484	Half solid; liquid amber colour.
14.	90·9	Neutral	,,	25	1091	1115	Solid.
15.	80·6	Acid	,,	25	—	1485	Nearly solid.
16.	80·6	Neutral	,,	25	—	1488	Nine-tenths solid; pale amber liquid.
17.	58·0	Acid	,,	—	—	1478	Very nearly solid.
18.	58·0	Neutral	,,	365	—	1477	A few crystals in bottom; liquid amber colour.

TABLE V.

Number of specimen.	Time in days.
1	127
3	225
2	281
4	324
5	350
10	611
11	692
14	1091
7	1096

From inspection it appears that the acid solutions crystallised earlier than the neutralised solutions of the same composition. Thus, the specimen containing—

90·9 per cent invert-sugar, acid, crystallised in 127 days.
90·9 ,, ,, neutral, ,, 281 ,,
80·6 ,, ,, acid, ,, 225 ,,
80·6 ,, ,, neutral, ,, 324 ,,
58·0 ,, ,, acid, ,, 350 ,,
58·0 ,, ,, neutral, did not crystallise.

Furthermore it appears that of these three acid solutions, the one containing the highest percentage amount of invert-sugar, 90·9, was the first one to crystallise; next in order of crystallisation was the specimen containing 80·6 per cent of invert-sugar; while the one lowest in invert-sugar, 58·0 per cent, was the last to crystallise.

To summarise, it appears that photo-crystallisation of partially inverted sucrose solutions, under conditions as here studied, progresses most rapidly the stronger the light to which the solutions are exposed and the greater the amount of invert-sugar which they contain.

When these three series of solutions were originally prepared the amount of inverted sucrose in the same was determined in the usual manner, as invert-sugar, by Fehling's solution. However, after completion of the work thus far described, it appeared desirable to submit all of the specimens to a more exact analysis in order to learn more about their constitution.

Acccordingly the sucrose, dextrose and levulose were, in each instance, individually determined. The author's method employed is here re-published (from the *School of Mines Quarterly*, xiii., No. 3); the $[\alpha]_D$ value of levulose is taken as $-93{\cdot}8$.

The Method.

Preparation of Solution.—If not already in solution, make of the sample to be examined a solution of arbitrary density. Of course, it goes without saying that this method is to be applied only in cases where no other optically active substances are present besides sucrose, dextrose, and levulose, and that care must be exercised that no preliminary treatment of the solution shall influence its original power of rotation.

The specific gravity of the solution above referred to is accurately determined by balance, and from this value there are calculated, in the following manner, the number of grms. of solution which contain 10·000 grms. of dry substance :*—

Ascertain the degree Brix corresponding to the specific gravity found. Divide 100 by the degree Brix; the quotient represents the number of grms. of solution which contain 1·00 grm. of dry substance. This value is multiplied by 10, and the product represents the number of grms. of solution, equivalent to 10·000 grms. of dry substance.

This amount is weighed out, placed in an accurately graduated 100 c.c. flask, and the solution in the flask is made up to 100 c.c. with distilled water.

The determinations to be made are as follows:—

Optical Examination.—Some of the solution is placed in a water-jacketed polarisation-tube, a thermometer is inserted in the solution, and a reading on this solution is taken in the polariscope, at the temperature of 20° C.

The reading thus obtained must be reduced to the basis of a reading made in a 100 m.m. tnbe.

Furthermore, if a sugar-polariscope has been used for the observation, the reading obtained must be transformed into circular degrees. With a polariscope using 26·048 grms. as the normal weight, the factor 0·346 is used for the sodium ray.

Gravimetric Determination before Inversion.—Of the 10 per cent solution weigh out an amount equivalent to 1·0 grm. of dry substance. Make this up to 150 c.c., and of this solution take 24·4 c.c., equivalent to 0·1628 grm. dry

* This concentration is chosen because the specific rotary powers of the sugars, values needed in the calculation of results, vary with the concentration.

substance. Take 50 c.c. of Fehling's solution,* heat to boiling; while boiling add the 24·4 c.c. of sugar solution, and boil for three minutes.

Then remove from flame, add cold distilled water, previously boiled, in order to cool the solution and prevent a further deposition of cuprous oxide.

Filter through a weighed asbestos filter, wash, first with boiling water, then with absolute ethyl alcohol, and finally with ether. Dry perfectly, cool, and weigh.

Calculate the cuprous oxide to its equivalent of metallic copper, and from the copper thus found ascertain the amount of sucrose corresponding.† From this figure the total reducing-sugars by adding 1/20 to the sucrose value indicated.

Gravimetric Determination after Inversion. — Of the original 10 per cent solution, weigh off an amount equal to 5·000 grms. dry substance; invert with 4 c.c. of concentrated HCl (specific gravity 1·20) by heating on boiling water-bath up to a temperature of 67° C. and maintaining the solution at that temperature for five minutes. Then remove the flask, cool it and its contents to the temperature at which the flask was graduated, and then make the solution up to 100 c.c.

Of the solution thus obtained take 20 c.c. and neutralise with sodium carbonate; then make up to a volume of 150 c.c. with distilled water; of this solution take 24·4 c.c., equivalent to 0·1628 grm. of dry substance, and proceed precisely as previously directed. Determine the value found, as before, from the table; the result obtained represents the total sugars present, *expressed as sucrose.* From this amount subtract the sucrose value found by prior determination,‡ and the difference represents the amount of sucrose actually present.

The results thus obtained represent :—the polarisation, in a 10 per cent solution, of the three sugars combined; the total reducing-sugars present; the amount of sucrose present.

In cases where the reducing-sugars—*i. e.*, the dextrose and the levulose together, exceed in amount the sucrose present, the gravimetric determinations before and after inversion should preferably be made according to E. Meissl's method for the determination of invert-sugar (*Zeitschrift des Vereines für Rübenzucker-industrie*, xxix., 1034, and E. Wein, *Tabellen zur Quantitativen Bestimmung der Zuckerarten*, Table No. IV).

(To be continued).

EVOLUTION OF CHEMISTRY IN THE LAST TWENTY YEARS.§

By Dr. A. LADENBURG.

(Continued from p. 198).

Turning now to subjects that concern us more immediately, we shall here first consider the progress that has been made in analytical chemistry by the application of electrolysis. The subject of electrolysis is a very old one, and so early as 1801 Cruickshank predicted that it would be turned to account in this way. It was qualitative analysis, however, that alone derived any benefit from it at first. Magnus afterwards drew attention to the fact that quantitative analysis—that is, the separation of the metals—must be possible by means of electrolysis; and experiments in the same direction were made, moreover, by Gibbs and by Luckow. Classen, Miller and Kiliani, Smith, Vortmann, and others, afterwards introduced the manifold applications of electrolysis to quantitative analysis; and Classen devised the form of apparatus by which the experiments are generally carried out. The great importance of the electromotive force was first recognised by Triliani and Le Blanc.

The applications of electrolysis to metallurgy are probably still more important. After the researches of Davy, it was especially those of Bunsen (published by the latter partly alone and partly in conjunction with Matthiessen) that brought about any notable advancement. Electrolysis first found a technical application upon the discovery of electrotyping by Jacobi and Spencer in 1839, an art which depends, however, upon an observation made by De la Rive in 1836.

The technical production of metals by electrolysis only became possible after the discovery, in 1872, of the dynamo-electrical machine, which was employed immediately thereafter (in the North-German Refinery at Hamburg) to remove copper from solutions. Other metals, such as zinc, magnesium, lead, silver, gold, &c., were also produced electrically afterwards. An operation of outstanding importance was the electrolytic production of aluminium, a metal which Bunsen first prepared by this method. The technical process of Heroult is different, however, from that of Bunsen, inasmuch as it is not a fused double chloride of the metal that is electrolysed, but aluminium oxide.

This is the place to refer to the great scientific and practical results that Moissan obtained as the outcome of his experiments with the electric furnace. Specially worthy of mention in this connection are the preparation of artificial diamonds; the production of calcium carbide (which had, however, been discovered long before by Wöhler) and of many other carbides; the preparation, in a state of purity, of chromium and of other difficultly fusible metals, &c. The first preparation of carborundum, which is also frequently attributed to Moissan, is due rather to Acheson, an American. Attention must be drawn to the facts that in many of these experiments electricity is only employed as a means of attaining to high temperatures (3000° to 4000°), and that the results can also be obtained in other ways, since the same high temperatures can, of recent years, be reached by means of chemical reactions. An entirely new branch of thermo-industry has thus arisen, by means of which great advances have already been made, and are still to be expected, in metallurgy. Of an earlier date is the employment of the oxy-hydrogen blowpipe in the melting and working of platinum, and so is the combustion of carbon and other elements (such as silicon, sulphur, phosphorus, &c.) in air or oxygen at high temperatures, for the purpose of attaining still higher temperatures; as, for example, in the blast furnace, or in the ingenious Bessemer process. The development of these methods by Goldschmidt, and their application to the production of metals such as chromium, manganese, iron, and nickel, free from carbon, and of a large number of alloys, are new however.

I must here recall the interesting results obtained, partly by Victor Meyer and partly by Crafts, by the application of the method of vapour density determination devised by the former. I regard as worthy of mention the proof that the molecule of iodine, I_2, breaks up at high temperatures into single atoms; and also the facts that the beginning, at least, of a similar dissociation has been ascertained in the case of bromine; that the molecule of arsenic, As_4, similarly splits into two; that potassium iodide even at high temperatures corresponds to the formula KI, and cuprous chloride to the formula Cu_2Cl_2, &c.

If the attainment of high temperatures has thus been of service for the purposes of our science and of technology, so likewise the endeavours, on the other hand, to obtain low temperatures have led to great advances, and to results of altogether unforeseen importance. In a preceding lecture, where the inter-relations of the

* Cupric sulphate cryst., 34·639 grms. in 500 c.c. H_2O; Rochelle salts, 173·000 grms. in 400 c.c. H_2O; Sodic hydrate, 50·000 grms. in 100 c.c. H_2O.

† Table published by the German Government, Law of 1887; also in Weichmann, Sugar Analysis, Table XI.

‡ That is, the amount as actually found by Table, prior to the addition of 1/20.

§ Read before the British Association (Section B), Dover Meeting, 1899.

states of physical aggregation and the significance of the critical temperature are referred to, the results of Pictet, of Cailletet, and of Wroblewsky on the liquefaction of the so-called permanent gases are stated. Of special importance were the detailed investigations of Wroblewsky and Olszewsky, who first obtained quantities of oxygen and nitrogen in the liquid state, and particularly described many of their properties. The mode of measuring temperatures by determining the potential of thermo-electric currents, which is now largely employed, also originated with them. In the experiments that have been carried out latterly, however, on the liquefaction of air and of other gases, Pictet's method has been abandoned again, and recourse has been taken to that of Cailletet (the latter method having been converted into a dynamical or continuous one); that is to say, the expansion of highly compressed gases has been employed in order that the necessary lowering of temperature may be effected. Thus Dewar, in his experiments upon the production of liquid air, liquefied, by its own expansion, air which was under a pressure of 100 atmospheres and was cooled by solid carbonic anhydride; whereas the recent technical method consists in cooling exclusively by expansion, and the effect of the latter is turned to account in a very ingenious manner by the employment of a self-intensive apparatus. Linde in Germany, and Hampson in England, almost at the same time, constructed technically efficient forms of apparatus, based upon this method, for the production of liquid air.

Liquid air has not as yet, however, found any technical application upon the large scale. Nearly pure oxygen is obtained from it very cheaply, and the attempt has been made to apply it in the technology of explosives, or to the production of high temperatures, but no ultimate pronouncement can be made with respect to this. Of far greater importance are the results that liquid air has achieved from a scientific aspect.

In the first place it must be mentioned that Dewar, by its aid, has succeeded in liquefying helium, and in obtaining air, hydrogen, and oxygen in the solid state; and that in doing so he has achieved almost everything that can be done in this direction. Dewar is at present engaged in trying to reach still lower temperatures by the aid of liquid hydrogen boiling under low pressure, in order to approach as nearly as possible to the absolute zero.

It is also of importance that ozone, which was obtained in the liquid state by Hautefeuille and Chappuis in 1882, by the aid of liquid ethylene, can easily be prepared in an approximately pure condition by the use of liquid air, so that Troost was able to determine its boiling-point and Ladenburg its density. The latter determination is of especial importance, since the molecular formula O_3, deduced from it, constitutes one of the most emphatic arguments in favour of the whole molecular theory; and this formula, which till then had only been supported by Soret's experiments, could not be regarded as finally settled.

But the results that have been furnished by this agency with respect to the discovery of new elements are of almost as great consequence.

When Lord Rayleigh compared the relative density of atmospheric nitrogen with that of nitrogen prepared from ammonia and other nitrogen compounds, he found a difference (in the third decimal place) which could not possibly be ascribed to an experimental error. He therefore resolved upon a minute investigation in order to find out the substance that was mixed with atmospheric nitrogen. This investigation he then carried out along with Ramsay, and it led to the discovery of argon, an element of which combinations are very difficult to be obtained. The molecular weight, deduced from the density, gave the number 39·92, and since, by Kundt's method, the monatomic character of the gaseous molecules was indicated, its atomic weight would be represented by the same number. The question as to the position of this element in the Periodic System is thereby rendered an extremely difficult one, since it falls near that of potassium and yet is beyond it.

Ramsay took up the problem from a very general point of view. It appeared to him highly probable that argon was a member of a whole group of elements, of which group he hoped to find additional members associated with nitrogen. It was thus that he came to investigate, amongst other things, the gases evolved from clèveite by heating with sulphuric acid, which Hillebrandt had considered to be nitrogen, and this led him to the discovery of helium. The brightest line in the spectrum of this gas, D_3 (D_1 and D_2 are the sodium lines), had been observed a long time previously by Lockyer in the spectrum of the sun's photosphere. Helium, whose atomic weight 4 was deduced from the density of the gas and from the rate of propagation of sound in it, was an analogue of argon in every respect; and it was thus clear to Ramsay that there must be another element which, with atomic weight about 20, should be placed before sodium, in the same way that helium comes before lithium, and argon probably before potassium (although the atomic weight of argon has been found, in the mean time, somewhat higher than that of potassium). A similar thing applies to tellurium, the atomic weight of which, according to the most recent determinations, is greater than that of iodine.

Ramsay now represents the further development of the subject as if the investigation, carried out with his utmost energy and effort, had remained unproductive, and as if an accident only had led him on to his further discoveries. There is in reality, however, no such accident in question, for the investigation of the residue from the evaporation of liquid air was only a link in the chain which, although perhaps unknown to himself, represented the course of his ideas. In this way he discovered crypton, the molecular weight of which was ascertained in a preliminary manner to be 45. It should probably be much higher, however, as the gas was still mixed with lighter gases, especially with argon. In the case of crypton, the ratio of the specific heats has also been ascertained to be 1 to 1·66, so that this gas is also a monatomic element, the position of which in the Periodic System is still undetermined.

As regards other discoveries, Ramsay found, by the systematic fractionation of argon (which he condensed by means of liquid air), three new substances which he considers to be elements. These are—Neon, with atomic weight 19·3 to 19·5, which is clearly to be placed therefore between helium and argon and before sodium; xenon, with density 65 (H=2) which might, as Ramsay supposes, be raised to 81 by further purification, so that it would be placed beyond bromine; and, finally, metargon, an easily condensable and even solidifiable gas, which shows the spectrum of carbonic oxide even after it has been mixed with oxygen and exposed for a long time to the passage of electric spark.

Even although all doubt as to the individuality and the elementary nature of these gases is not yet removed, still these investigations are unquestionably amongst the most successful that have been carried out during the last twenty years. Liquid air served not merely as starting material for the investigations, but Ramsay also employed it, or at least the liquid oxygen obtained by its aid, in an ingenious manner for the purpose of separating the various new elements.

The question as to the position of these "elements" in the periodic system has been much discussed, and up to the present it is not finally solved. On the other hand, we may now say that even if our views respecting the connection between the properties of the elements and their atomic weights should be modified on account of these newly discovered facts, still the periodic law has rendered excellent service as an invaluable guide in this obscure region.

Although such unexpected discoveries were thus made, still they will not exercise any considerable influence upon

chemistry as a whole, since all these elements apparently resemble argon, and do, probably, not give many combinations. Hence it may be said that these interesting investigations will probably not prove of great significance as regards their consequences, and that in this respect they will fall short of other researches which have not excited the interest of such wide circles.

I merely recall here the isolation of fluorine by Moissan in 1886, the discovery of $Ni(CO)_4$ and analogous compounds by Mond in 1890, and pass on to consider more particularly the investigation of the chemistry of nitrogen, which has made great advances in recent years.

The discovery of hydroxylamine, by Lossen, falls under review here, although, of course, it took place at a much earlier date (in 1865). It has not been referred to previously, however, since its importance only came to be recognised gradually, a result to which Victor Meyer's researches on the oximes and their stereo-isomerism materially contributed.

The preparation of phenylhydrazine, by Emil Fischer, also falls to be mentioned here. It must be looked upon as of outstanding importance, on account of its leading to the clearing up of the sugar group. Following upon this there are the valuable researches of Curtius, who discovered hydrazine in 1889 and hydrazoic acid in 1890. The utilisation of these two substances has already led to numerous investigations, and will lead to others. As worthy of mention I also refer to the researches of Thiele, who (amongst others) found out a convenient and technically practicable method for the manufacture of hydrazine; and to those of Raschig, who cleared up the nitrogen-sulphonic acids, and in doing so discovered the method now employed for the production of hydroxylamine.

It does not seem to me that this is the place to enter more fully into this subject, since I am really giving a historical sketch, in which only those things that are of general importance can be prominently brought forward.

I may thus recall here a discovery of Hellriegel's which marks an epoch in chemistry and agriculture. According to Hellriegel, leguminous plants, and lupins in particular, possess the power of assimilating, with the aid of lower organisms, the nitrogen of the air. In this connection the fact must not be passed by without mention that Berthelot had previously asserted the assimilation of free nitrogen.

An observation which is to a certain extent of an opposite character is the proof furnished by Buchner that fermentation is possible even without living organisms, by means of the liquid expressed from yeast (zymase).

More particular consideration may be given to a research by van 't Hoff, in which the idea and the significance of the transition temperature are clearly stated. Van 't Hoff is led to the idea by the comparison of chemical reactions with the transitions from one of the states of physical aggregation to the others; but the same conception may be arrived at by the aid of the phase rule.

(To be continued).

Compounds of Formic Aldehyde with Menthol and Borneol.—A. Brochet.—The formals obtained have the general form $CH_2(OR)_2$. Dimentholic formal is a white solid body with a rather agreeable odour, insoluble in water, but very soluble in ether and benzene. It is hardly soluble in cold alcohol, but is miscible in warm alcohol; it crystallises in long, fine, silky needles, which felt very easily; its melting-point is 56·5°. Diborneolic formal is a solid white body smelling somewhat of borneol; it is very soluble in ether and benzene, and crystallises in alcohol in pearly flakes; it is fusible at 166°, and distils without decomposition at 344—345°.—*Bull. Soc. Chim.*, Series 3, xxi., No. 8.

NOTICES OF BOOKS.

Examination of Water for Sanitary and Technic Purposes. By Henry Leffmann, M.D., Ph.D. Fourth Edition, Revised and Enlarged, with Illustrations. Philadelphia: P. Blakiston's Son and Co. 1899. Pp. 145.

Only a few changes have been made in this edition, these being principally improvements in detail. The principal advance in water examination since the last edition has been in bacteriological methods. It is freely admitted that the detection of pathogenic microbes in water is so difficult as to be rarely accomplished; it is therefore, we think, greatly to be desired that in any report condemning a water on pathogenic grounds, details of the method of examination and identification of the microbes should be given in full, so that there may be no question as to the accuracy of the report.

We cannot accept Dr. Leffmann's statement that "it is now generally admitted that mere microbe-counting is of little use in judging of the sanitary value of water-samples" without a slight demur: the actual *number* of microbes found does not of course imply much, but a competent man who is accustomed to handle numbers of samples can form a very good opinion of the character of the water-samples by the variation in the numbers of the colonies present.

The author deals with the whole range of water analysis, the section on interpretation of results being of special interest and value.

Laboratory Manual. Experiments to Illustrate the Elementary Principles of Chemistry. By H. W. Hillyer, Ph.D. New York: The Macmillan Company. 1899. Pp. 200.

In Part I. of this volume the preparation and properties of the commoner elements and their compounds are described, together with experiments illustrating the fundamental ideas of Chemistry; and Part II. deals with the verification of the Quantitative Laws. As a text-book it will no doubt fulfil its object; it has, however, one feature to which we must take exception—only one side of each sheet is printed on, the other being left blank; we can see no advantage in this course, and, considering that all these blank pages are numbered, the book appears to have double the number of pages—viz., 200—that it in reality possesses, viz., 100.

Lexicon of the Carbon Compounds. (Lexikon der Kohlenstoff-Verbindungen). By M. Richter. In 35 Parts. Hamburg and Leipzic: Leopold Voss. 1899. Parts 1 to 12, pp. 784.

We cannot but admire the steady and untiring perseverance shown by the author in plodding through the stupendous task he has undertaken—a task apparently hopeless on account of the continuous and ever-increasing additions which are constantly being made to our knowledge of the carbon compounds.

The work of tabulating the carbon compounds was originally commenced in the year 1883, under the title of "Tables of the Carbon Compounds," the compilation of the present "Lexicon" being undertaken fn the year 1889, but much delay was occasioned by the work of the Geneva Commission concerning the nomenclature of the aliphatic hydrocarbons in 1892, while the number of registered compounds has increased during the progress of the work from 16,000 to about 65,000 carbon compounds at the present day.

The arrangement of the material and the manner of registering it remains the same as in the original "Tables of Carbon Compounds," but the Tables of Percentages have been extended to the forms CHO, CHN, and CHON, altogether to about 20,000 formulæ.

When complete these volumes will be of immense value to workers in organic chemistry as a book of reference, and too much praise cannot be given to the author for his long and patient labour in compiling such a work,

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The Foundations of General Chemistry. (Grundriss der Allegemeinen Chemie). By W. Ostwald. Third Edition, Enlarged, with 57 Illustrations. Leipzic: Wilhelm Engelmann. 1899. Pp. 549.

As its title indicates, the general tone of this volume is entirely theoretical, and the subject certainly is treated in a masterly manner.

The book is divided into two principal parts, and eleven books, each consisting of four or more chapters. The first part deals with stochiometry, and the second with relationships between the properties of elements, such as chemical energy, thermochemistry, electrochemistry, photochemistry, &c. There are two comprehensive indices, one of names and the other of subjects.

The book is well arranged, and will prove invaluable to both students and more advanced chemists.

Chemical Industry. (La Chimica Industriale).

We have received the first two numbers of this new Italian Journal, published in Torino, which is the official publication of the Italian Society of Chemical Industry. The subject matter consists of articles, abstractions, notes, trade notices, &c., filling sixteen pages; it is well printed, and on much better paper than is usually found in continental journals. We wish our new contemporary every success.

The Chemical Trade Directory. Manchester: Davis Brothers. 1899. Pp. 374.

The compilers of this Directory have aimed at producing a volume which will be of interest and practical use to chemical manufacturers, merchants, agents, brokers, assayers and analysts, &c., in Great Britain and Ireland.

The first three sections—comprising chemical manufacturers, chemical merchants, and makers of plant and material—are compiled from information obtained directly from the firms and individuals concerned. The list of analysts and public samplers will doubtless prove to be of much use, as it often occurs that in cases of dispute the parties to the dispute are unaware of the existence of an analyst or sampler in their neighbourhood, and valuable time may therefore be lost. We congratulate Messrs. Davis Bros. on the production of a very useful volume.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 16, October 6, 1899.

Production of Ozone during the Decomposition of Water by means of Fluorine.—Henri Moissan.—The action of fluorine on water affords a new proof of the easy polymerisation of oxygen to form ozone at a low temperature. The experiments which the author performed in 1891 are now repeated with a larger volume of fluorine, prepared in a copper apparatus. The current of fluorine is led into the water through a small platinum tube—the water being kept at 0°. Attached to the vessel is a bulb into which the liberated gas passes. When the bulb is full by displacement of the ozonised oxygen, the contents are estimated by means of a solution of potassium iodide in presence of excess of sulphuric acid. The iodine liberated by the ozone is titrated with sodium thiosulphate solution. As much as 143·9 c.c. of ozone was found per litre.

Atomic Weight of Boron.—Henri Gautier.—Of all the non-metallic elements, boron is the one whose atomic weight is the least certain. Since the preparation of pure amorphous boron by M. Moissan, the author has redetermined the atomic weight by employing two compounds of small molecular weight, boron sulphide and boron carbide; both these substances being prepared from pure amorphous boron. The mean of four determinations gives the atomic weight as 11·041, with a probable error of 0·017.

Anhydrous Magnesium Carbonate.—R. Engel.—During a former research on the carbonates of magnesium, the author observed that, when heating the double sesquicarbonate of magnesium and potassium under favourable conditions, there results a mixture of normal potassium carbonate and anhydrous magnesium carbonate. This latter compound differs in many respects from the natural carbonate, especially in its solubility in water and the ease with which it combines with water. It is best prepared by heating the double carbonate of magnesium and ammonium.

Heat of Oxidation of Tungsten.—MM. Delépine and Hallopeau.—The authors have measured the heats of combustion of tungsten and of the suboxide WO_2, in order to compare these numbers with those obtained for other metals, and so to assign a place to tungsten in the series of elements. The numerical results are shown by the following equations:—

$$W + O_3 = WO_3 + 195{\cdot}41 \text{ cal. at constant volume}$$
$$\text{and } + 196{\cdot}3 \text{ cal. at constant pressure.}$$

$$WO_2 + O = WO_3 + 64{\cdot}63 \text{ cal. at constant volume}$$
$$\text{and } + 64{\cdot}9 \text{ cal. at constant pressure.}$$

$$W + O_2 = WO_2 + 131{\cdot}4 \text{ cal.}$$

Action of Potassammonium on Arsenic.—C. Hugot.—The author, continuing his research, considers two further cases:—(1) When the ammonium alkali is in excess, a yellow amorphous body is formed, slightly soluble in liquid ammonia gas, to which it imparts a yellow colouration. Under pressure and at ordinary temperatures it becomes brick red, analysis showing it to have the formula $AsK_3.NH_3$. (2) When the arsenic is in excess, a red liquid is formed, which, after being filtered through glass-wool and evaporated, leaves an orange-coloured mass. This compound appears to have the formula $As_4K_2.NH_3$. When heated to a little below 300° it loses its molecule of ammonia gas, and becomes red in colour.

Action of Bromine on some Derived Chlorated Compounds of Benzene in presence of Aluminium Chloride.—A. Mouneyrat and Ch. Pouret.—Very little is known about the chlorobromate compounds of the aromatic carbides. The authors' research was undertaken in order to find out whether there is a general method of preparation of these compounds, *i.e.*, whether the action takes place according to the equation—

$$C_6H_mCl_n + Br_p = C_6H_{(m-p/2)}Cl_n + (HBr)_{p/2}.$$

Experiment has verified this hypothesis, and the following compounds have been prepared:—

C_6Br_5Cl	melting at	299—300°
$C_6Br_4Cl_{(1)}Cl_{(4)}$	,,	278—278·5°
$C_6Br_3Cl_{(1)}Cl_{(2)}Cl_{(4)}$	,,	260—261°
$C_6Br_2Cl_{(1)}Cl_{(2)}Cl_{(4)}Cl_{(5)}$	,,	246—246·5°
$C_6Br_4 < \begin{matrix} CH_{(3)} \\ Cl_{(4)} \end{matrix}$	,,	258—259°

Berichte der Deutschen Chemischen Gesellschaft.
February 13, 1899.

Contribution to the Study of Hydroxylamine.—S. Tanatar.—Hydroxylamine acts sometimes as an oxidising and sometimes as a reducing agent. If an aqueous solution of hydrochlorate of hydroxylamine is saturated with sulphurous acid gas, acid sulphate of ammonium is obtained almost quantitatively, $H_2SO_3+NH_2OH.HCl=NH_4.HSO_4+HCl$. Perchloride of phosphorus reacts slowly in the cold, and rapidly when heated on hydrochlorate of hydroxylamine, giving chloride of ammonium, nitrogen, and oxychloride of phosphorus. Peroxide of hydrogen reacts on a solution of hydrochlorate of hydroxylamine heated to 50°; it gives off nitrogen and oxygen, while a part of the hydroxylamine is transformed into nitric acid.

Action of Malonate of Ethyl on Oxide of Mesityl.—D. Vorlaender.—According to the author, the acid melting at 148° obtained by combining oxide of mesityl and malonic ether and saponifying the oily ether formed, is identical with dimethylhydroresorcin, $(CH_3)_2\begin{cases}CH_2-CO\\ \\ CH_2-C-OH\end{cases}\!\!>CH$, which has already been described.

On 1.9-Dimethyluric Acid and 1.7.9-Trimethyluric Acid.—E. Fischer and F. Ach.—There were five dimethyluric and three trimethyluric acids already known; according to theory, there should be six of the former and four of the latter. The authors have succeeded in preparing the other two. The 1.7.9-trimethyluric acid was prepared by treating a warm solution of methyl-9-amino-6-oxy-8-chloro-2-purine with nitrite of sodium. The crystalline powder obtained corresponds to the formula $C_6H_5N_4O_2Cl,O.5H_2O$, soluble in boiling alkalis, forming salts; slightly soluble in water, alcohol, and acetic acid. This compound melts at about 310—320° with decomposition. The dimethyl 1.9-uric acid is obtained by condensing the corresponding methyl-9-dioxychloropurine with formaldehyde in the presence of dilute potash; it is precipitated in the form of a slightly soluble potassium salt. By treating this salt with iodide of methyl at 80°, dimethyl-1.9-dioxy-6 δ-chloro-2-purine is obtained, and this body, when heated for four hours to 100° in a closed vessel with concentrated hydrochloric acid, gives dimethyl-1.9-uric acid, crystallising in rectangular tables melting with decomposition at about 400°.

Observations on the Purine Group.—E. Fischer.—This paper consists of a number of separate observations which contribute to our knowledge of the constitution of the purines. When an alcoholic solution of methyl-9-trichloropurine, saturated with ammonia gas is heated to 100° a mixture of methyl 9-dichloradenine and methyl-9-amino-8-dichloro-2.6-purine is obtained. Dimethyl-3.9-uric acid, heated with perchloride and oxychloride of phosphorus to 145—155° for six or seven hours gives methyl-9-oxy-8-dichloro-2.6-purine, fusible at 272—273°. Oxychloride of phosphorus reacts at about 140° in a closed vessel on methyl-7 uric acid, giving methyl-7-oxy-8-dichloro-2.6-purine. This latter, in its turn, furnishes methyl-7-trichloropurine when heated to 155—160° for five hours with a mixture of perchloride and oxychloride of phosphorus.

Action of Hydrochloric and Hydrobromic Acids on the Aromatic Nitroso-derivatives.—E. Bamberger, H. Busdorf, and B. Szolayski.—Hydrochloric acid transforms nitrosobenzene first into phenylchlorhydroxylamine, $C_6H_5N<^{OH}_{Cl}$; this body becomes rapidly isomerised, giving *p*-chlorophenylhydroxylamine, $Cl.C_6H_4.NHOH$. The action of hydrobromic acid on nitrosobenzene is entirely analogous. The results are also analogous with *p*-nitrosotoluene, but cresols are obtained in addition.

Products of Condensation of Formic Aldehyde with Quinaldine.—W. Kœnigs.—Quinaldine will unite with 1, 2, or 3 molecules of formic aldehyde. The 3 atoms of hydrogen of the methyl group united with the nitrogen are replaced successively with 1, 2, or 3 CH_2OH-groups, forming α-quinolylethanol, $C_9H_6N.CH_2.CH_2OH$; α-quinolylpropanediol, $C_9H_6N.CH(CH_2OH)_2$; and α-quinolylbutanetriol, $C_9H_6N.C(CH_2OH)_3$.

Bulletin des Travaux de la Société de Pharmacie de Bordeaux, May, 1899.

This issue contains no chemical matter.

June, 1899.

On a Coloured Reaction of Alcaptone.—G. Denigès.—In the presence of persulphate of ammonium or the peroxides of lead and manganese in alkaline solution, alcaptone (homogentisic acid) gives a very marked reddish brown colouration, even when present in very small quantity. For its detection in urine, 0·5 to 1 grm. of oxide of lead is placed in a test-tube with 10 c.c. of the urine, and three or four drops of potash or soda-lye; this should be well shaken up for a few minutes and filtered. If the urine is normal its colour remains unchanged, but if alcaptone is present it becomes distinctly red. If peroxide of manganese is used instead of peroxide of lead, the colour will be more inclined to brown.

On Effervescing Water, so-called "Seltzer."—P. Carles.—The author points out that very often insufficient care is exercised from the hygienic point of view in the manufacture of so called "mineral waters," such as seltzer, &c. The three principal things to take note of are:—(1) The judicious choice of a soft water; (2) to use only perfectly pure carbonic acid; and (3) not to allow the use of valves made partially of lead. He points out that it has been shown by Duclaux that, in times of epidemics, chance is the principal factor which governs the bacteriological purity of the water, and that the microbes of typhoid, for example, will live for a longer time in seltzer water than in ordinary tap-water or distilled water.

July, 1899.

Glycerophosphate of Lime.—P. Carles.—It is generally admitted that, of the glycerophosphates, that of lime is the one to be preferred. This, however, is not very soluble; its coefficient of solubility being from 3·3 to 6 per cent according to different authors. The author has endeavoured to account for this rather wide variation. He found that the maximum of solubility of the crystallised neutral glycerophosphate of lime was reached at 28°; if the temperature be increased above this point, the solubility rapidly decreases, and it becomes almost insoluble again. He confirms the results of other writers, that the addition of a little acid greatly increases the solubility of the salt, but he does not recommend the use of citric acid, as an insoluble citrate of lime is gradually formed; oxalic acid gives much better results. One hundred grms. of the neutral powdered glycerophosphate should be added to 800 grms. of warm water; 30 grms. of oxalic acid is then dissolved in 100 grms. of boiling distilled water. These two solutions must be thoroughly mixed and filtered; the precipitate is washed until the filtrate is one litre in volume. The solution is perfectly clear, and contains no trace of oxalic acid, and is also very stable, even after prolonged heating on the water-bath.

Volumetric Estimation of Aniline by Bromine and Bromine by Aniline.—G. Denigès.—Already noticed in this column.

The presence of Estragol in Essence of Chervil.—E. Charabot and L. Pillet.—The authors have examined a quantity of freshly sown chervil (*Chærophyllum sativum*), from which they obtained 4·25 grms. of essence in the form of a pale yellow oil. The result of their experiments with, and analysis of, this oil shows that estragol is the principal constituent of essence of chervil.—*Bull. Soc. Chim.*, Series 3, xxi., No. 8.

MISCELLANEOUS

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th instant, His Grace the Duke of Northumberland, K.G., President, presiding. The following were elected members:—H.H. The Thakore Saheb of Gondal, G. F. Barrett, J. B. Broun-Morison, A. H. Savage Landor, and T. C. Porter. The special thanks of the Members were returned to "A Lady Member" for her donation of £100, and to Mr. George Matthey, F.R.S., for his donation of £100 to the fund for the Promotion of Experimental Research at Low Temperatures. The special thanks of the Members were returned to Miss Elinor Busk and Miss Frances Busk for a portrait of Mr. George Busk, F.R.S., Treasurer of the Royal Institution from 1873 to 1886.

Merck's "Digest," Nos. 4 and 5.—These two numbers deal respectively with tannoform and largin. The former is a condensation product of tannin and formic aldehyde, having the formula $C_{29}H_{20}O_{18}$. It occurs as a loose reddish-white powder, insoluble in water, but soluble in alcohol, ammonia water, and solution of soda or sodium carbonate; it melts with decomposition at 230°. It is recommended as a perfectly safe and innocuous antihidrotic and antiseptic siccative; compared with salicylic acid it is said to be more pleasant and more efficacious. Largin is an albumen and silver compound, the albumenoid component of which is protalbin, a new derivative of the para-nucleo-proteids. The preparation is a whitish-grey powder, soluble in alcohol, 10·5 per cent of which is taken up by water at the ordinary temperature; it possesses powerful bactericidal properties, and will easily penetrate tissues.

MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Society of Arts, 8. Opening Address of the 146th Session, by Sir John Wolfe Barry, K.C.B., V.P.Inst.C.E., F.R.S.

THURSDAY, 16th.—Chemical, 8. "The Chlorine Derivatives of Pyridine—Part IV., Constitution of the Tetrachloropyridines," by W. J. Sell, M.A., and F. W. Dootson, M.A. "Contributions to our Knowledge of the Aconite Alkaloids—Part XV., On Japaconite, and the Alkaloids of Japanese Aconite." by W. R. Dunstan, F.R.S., and H. M. Read. "On the Determination of Transition Temperatures," by H. M. Dawson, Ph.D., and P. Williams, B.Sc.

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MICHAELMAS TERM.—Monday, October 2, to Saturday, December 16.
LENT TERM.—Monday, January 8, to Saturday, April 7.
EASTER TERM.—Monday, April 30, to Saturday, July 28.

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THE CHEMICAL NEWS.

Vol. LXXX., No. 2086.

A BIBLIOGRAPHY OF STEEL-WORKS ANALYSIS.

By HARRY BREARLEY.

With the intention of realising what changes had taken place in steel analysis since analytical chemistry became adapted to steel-making, I began with volume I. of the Chemical News, and, without pretending to read—much less study—scanned its pages, noted the volume, page, and author of the articles I was likely to be interested in, and read a particularly interesting paper here and there. These references, put in order, have been of great service whenever difficulties or doubts have cropped up. Many helpful details were at once made use of. Many series of lectures and investigations by Faraday, Tyndall, Odling, Frankland, Miller, Crookes, Percy, Calvert, Letheby, Angus-Smith, Forbes, and a number of others, are comprehensive demonstrations of every-day phenomena, of physical and chemical laws, or models of prolonged and delicate investigations. To the hundreds of half-educated analysts who, like myself, were not prepared for the work, but eagerly accepted it as the best available means of earning a living, a better and more practicable way could hardly be recommended of shaking off blear eyes and narrowness, and of learning patience and perseverance and reverence.

The above form of indexing, together with frequent experiment, has led to a bibliography of a partial kind, which, although particularly valuable to myself, may be of considerable value to others also. It refers to every element usually estimated in the materials generally examined in a steel works laboratory.

The compilation, with few exceptions, is made from the following readily accessible journals:—

The Chemical News, 1860 to 1899, vols. i. to lxxix.
The Journal of the Chemical Society, 1885—1898, vols. xlvii. to lxxiv.
The Journal of the Iron and Steel Institute, 1880 to 1899.

Owing to the numerous reprints and abstracts these journals contain, the area covered is a very large one. The source of the reprint or abstract is not given here. I am sorry to have had no opportunity of examining other English journals, particularly the *Journ. Soc. Chem. Industry*, but hope to do so for some of the rarer elements whose modes of estimation are neither so numerous nor so well established as is that of carbon or manganese.

Fresenius's "Quantitative Chemical Analysis" abounds in references, but they are mainly to foreign journals not easily accessible, and, providing they were, there are enough analysts unable to read either German or French to make a supplementary reference to an English reprint, or even abstract of the paper referred to, of considerable value in an English translation of that admirable treatise.

The following synopses illustrate lamentable differences in the working of the same process. If every steel works laboratory could be stimulated to observation with experiment, there would soon be fewer such disagreeable discrepancies and direct contradictions. Lord Rayleigh's philosophy, if taken to heart, would do a great deal in this direction. "One's instinct at first is to try to get rid of a disagreeable discrepancy; but I believe that experience shows such an endeavour to be a mistake. What we ought to do is to magnify a discrepancy with a view of finding out the explanation" (*C. N.*, lxxi, 300).

There is a little indefiniteness about the classification of the means of estimating an element. Some marked feature, such as the final state, has had to be fixed on, although the most diverse processes may lead up to it.

A number of papers have been neglected, on the ground that they contain only commonplace information or points which are already well covered by the papers noticed. Such bibliographical errors are inseparable from a synopsis made to assist one in every-day operations and chiefly for personal use.

If an English reprint of a paper is available, that is referred to. Where there is an abstract only, reference is commonly made to one journal only. In many cases a similar abstract may be found in the corresponding volume of the other journals.

MANGANESE.

The following classification is adopted:—

I. Separating the Iron.
  a. Precipitating the Iron.
    1. As Acetate. 2. Sulphate. 3. Phosphate. 4. Hydrate. 5. Other Reagents.
  b. Precipitating the Manganese.

II. Separating other Elements.

III. Gravimetric Estimation of Manganese.
  a. As Mangano-manganic Oxide.
  b. As Manganese Pyrophosphate.
  c. As Manganese Sulphate.
  d. As Manganese Sulphide.
  e. As Manganese Carbonate.
  f. Electrolytically.
  g. Miscellaneous.

IV. Volumetric Estimation of Manganese.
  a. Titrations with Standard Permanganate.
  b. Oxidations to Permanganate.
  c. Oxidations to Higher Oxides of Manganese.
    1. The Chlorate Process.
    2. Other Oxidimetric Processes.
    3. Available Oxygen in Ores, &c.
  d. Indirect Processes.
  e. Miscellaneous Processes.

V. Detection of Manganese.

VI. Miscellaneous Notes.

I. Separation of Iron.

a.1. *Precipitating the Iron with Acetate (Succinate or Formate).*—

1. Kessler (*C. N.*, xxvii., 14).—Explains the state of a solution of ferric chloride when soda carbonate is added to faint precipitation. Imperfect separations are due to excess of acetate; a minimum quantity stated.
2. Rosenthal (*C. N.*, xxxvi., 147).—A re-precipitation by the acetate process is quite unnecessary.
3. Jewett (*C. N.*, lx., 273).—Five per cent free acetic acid causes complete separation when large amounts of soda acetate are used. The same is true for zinc and nearly so for Ni and Co.
4. Meinecke (*J. C. S.*, lvi., 309).—The successful separation depends on perfect neutralisation, small amounts of acetate and acetic acid, and short rapid boiling.
5. Brearley (*C. N.*, lxxv., 13).—Free acetic acid corrects errors due to large excesses of acetate. Separations complete with one precipitation without free acetic if small amount of acetate is used.
6. Riggs (*J. C. S.*, lxii., 536).—There is danger of a little Mn separating as higher oxide when the solution is neutralised previous to acetate separation.
7. Tamm (*C. N.*, xxvi., 37).—Precipitates with succinates. Objects to oxidation of iron with HNO_3, because part of the Mn is then always in Mn_2O_3 state and precipitated with the Fe; recommends $KClO_3$, or evaporation of HNO_3 entirely.

8. Fresenius ("Quant. Anal."). — Basic formates are more easily washed than acetates. Succinates are said to completely precipitate Al along with the Fe. (Basic acetate separations will be more fully treated under "Nickel").

I.*a*. 2. *Precipitating the Iron with Sulphates.*—

9. Kessler (*J. I. S. I.*, 1880, 353).—Mixed chlorides are thoroughly neutralised with Na_2CO_3; the diluted solution is precipitated in the cold with Na_2SO_4, and straightway filtered. (A translation of this paper appears in *Iron*, May 31, 1879).

10. Meinecke (*J. C. S.*, lvi., 310).— Precipitates with $(NH_4)_2SO_4$ at ordinary temperatures. Mn, Ni, Co, Cu, and Zn are in solution, and Al partly.

11. Rurup (*J. I. S. I.*, 1896, i., 535).—Solution neutral, but no definite precipitate; 18 c.c. 10 per cent Na_2SO_4 precipitates 4 gms. Fe in the cold; filtrate titrated with permanganate.

I.*a*. 3. *Precipitating the Iron with Phosphates.*—

12. Bloxam (*C. N.*, l., 112).—Speaks unfavourably of the acetate process.* Precipitates neutralised iron solution with ammonium acetate and excess of soda phosphate; ferric phosphate re-dissolved and re-precipitated; Mn in filtrate estimated as $Mn_2P_2O_7$.

I.*a*. 4. *Precipitating the Iron as Hydrate.*—

13. Sarnstrom (*C. N.*, xlvii., 177).—Preparatory to estimating the Mn by Guyard's process, the Fe is precipitated by a small excess of soda bicarbonate. (See 95, 96, and 97).

14. Meinecke (*J. I. S. I.*, 1888, ii., 326).—Fe solution saturated with CO_2, neutralised with soda bicarbonate, and carefully coagulated with a drop more. Precipitate free from Mn, Co, and Ni. Process not available in presence of much Al. Phosphate method of precipitating Fe worthless; precipitation with HgO of little use; $BaCO_3$ always leaves Mn in precipitate. See also *J. C. S.*, lvi., 310, for separation of other elements by a similar process.

15. Fresenius ("Quant. Anal.," p. 437, 7th ed.).—Add ammonium carbonate so that fluid loses its transparency and tends to become more turbid rather than otherwise, then boil; the iron is precipitated. Described also by Dittmar ("Quant. Anal.," p. 74). Known as Schwarzenberg or Herschell's method.

I.*a*. 5. *Iron Precipitated by various Reagents.*—

16. *Zinc Oxide.*—Volhard (*C. N.*, xl., 207; *J. I. S. I.*, 1880, 355).—Dilute H_2SO_4 solution of the metals neutralised with soda carbonate; emulsion ZnO added until complete precipitation of Fe is indicated by sudden coagulation of the solution.

17. *Ammonium Chloride.*—Kern (*C. N.*, xxxiii., 90).—$Fe_2Cl_6 + MnCl_2$ precipitated with KHO, large amount $(NH_4)Cl$ added and boiled; the filtrate contains the Mn. It is further precipitated as sulphide and estimated as sulphate.

Kern (*C. N.*, xxxv., 270).—Powdered sample mixed with $(NH_4)Cl$ and strongly ignited; process repeated until Fe is volatilised. Residue separated from SiO_2, &c., is weighed as Mn_3O_4 (see 58).

18. *Barium Carbonate.*—Forbes (*C. N.*, xvi., 105), and Juptner (*J. I. S. I.*, 1885, i, 247), separate Fe with $BaCO_3$ (see 14).

19. *Chlorine.*—Kern (*C. N.*, xxxv., 247).—Precipitate Fe and Mn together with ammonia. Volatilise Fe in current of Cl; estimate residue as Mn_3O_4.

19*a*. Friedmann (*J. I. S. I.*, 1888, ii., 328).—Volatilise Fe in Cl. Graphite, Cu, Co, Ni, Mn, and slag in the residue.

20. *Sulphuretted Hydrogen.*—Carnot (*J. I. S. I.*, 1887, i., 470).—Acetate added to neutralised solution and H_2S passed through; Fe, Ni, and Co are completely precipitated.

21. *Lead Carbonate.*—Campbell (*J. C. S.*, lxii., ii., 103) —Ferric solutions are precipitated by $PbCO_3$. Mn, Co, Ni and ferrous salts are not decomposed. Warming assists the reaction; nitrate should be absent.

22. *Lead Oxide.*—Field (*C. N.*, i., 4).—Mn, Ni, and Co are separated from Fe by precipitating with this reagent.

23. *Soda Nitrite.*—Wynkoop (*J. C. S.*, lxxiv., ii., 54).—Fe, Cr, Al are completely separated from Mn, Zn, Ni, Co, by boiling with excess of $NaNO_2$. It is best to have Fe in the ferrous state.

24. *Ether.*—Skey (*C. N.*, xvi., 201) suggests a separation by abstracting the Fe with ether from a solution of the sulphocyanides.

25. *Nitroso-β-naphthol.* — Knorre (*C. N.*, lix., 232; *J. I. S. I.*, 1887, i., 470).—Fe must be present as sulphate or chloride; neutralised solution precipitated with at least ten times as much of the reagent, dissolved in acetic acid, as there is Fe present. By the same process Fe is separated from Cr, Ni, Zn, and Al. See also De Koninck, Chem. News, lxii., 19

26. Burgass (*J. C. S.*, lxxii., ii., 162).—Nitroso-β-naphthol precipitates, Cu, Co, and Fe completely; Mn, Hg, Ni, Cr, Pb, Zn, Al, Cd, Mg, Ca, Bi, Sb, and As remain in solution.

27. *Electrolytic.*—Koeppel (*J. C. S.*, lxxiv., ii., 354).—Solution of Fe and Mn sulphates are poured into boiling soda pyrophosphate. The Fe is deposited from the clear solution.

I.*b*. *Precipitating the Manganese.*—

28. Beilstein and Jawain (*C. N.*, xl., 300; *J. I. S. I.*, 1880, 354).—Solution of the metals poured into concentrated KCN; the Mn is precipitated with iodine and converted into sulphide. Describes also the chlorate process, which is really a separation in which the manganese is precipitated.

29. Moore (*C. N.*, lvii., 125).—Sodium carbonate in excess added to concentrated solution of the metals; dissolve precipitate in KCN, add a little KHO, and precipitate Mn with H_2O_2. The Mn may also be precipitated with H_2S. Ni and Co are also precipitated.

30. Classen (*C. N.*, xl., 33).—Manganous solutions are precipitated by neutral potassium oxalate; the precipitate being soluble in excess. The potassium manganous oxalate is decomposed by concentrated acetic acid, but the potassium ferric oxalate remains dissolved. Zn or Mg chlorides, used to obviate influence of alkaline chlorides. The process separates Ca, Co, Ni, and Cu from Fe and Al, and is later elaborated (*C. N.*, xl., 196) to cover a number of other separations.

31. Blum (*C. N.*, lv., 236).—HCl solution of chlorides mixed with tartaric acid, so that no precipitate is formed with ammonia; ferricyanide added. Mn, Ni, Co, and Zn are precipitated. Filters badly.

32. Engels (*J. C. S.*, lxxiv, ii., 192).—MnO_2 is precipitated by the electric current from an acidulated solution of the sulphates.

(To be continued).

* "The advocate of one method often makes the other suffer by comparison, more by reason of his own want of skill in the manipulation of the other method than by reason of any great advantage in his own" (Blair, *C. N.*, lvi. 246).

Christmas Lectures at the Royal Institution.—The Annual Course of Christmas Lectures, specially adapted for young people, at the Royal Institution, will this year be delivered by Mr. Charles Vernon Boys, F.R.S. The subject will be "Fluids in Motion and at Rest." The Lectures (which will be six in number) will commence on Thursday, December 28, at Three o'clock. The remaining Lectures will be delivered on December 30, and on January 2, 4, 6, and 9, 1900.

METHOD FOR THE ESTIMATION OF SILICON IN FERRO-CHROMIUM, AND OF SILICA IN CHROME ORE.

By GEORGE TATE, Ph.D., F.I.C.

One to two grms. of ferro-chromium or of ore are fused with about five times their weight of sodium peroxide in a nickel crucible. The crucible and contents, after cooling, are brought into water contained in a capacious nickel dish. The alkaline liquid so obtained containing chromate and silicate, together with oxides of iron and nickel in suspension, is treated with hydrochloric acid in quantity insufficient to neutralise the alkali, and then evaporated to dryness in the nickel dish. The residue is scraped, as far as is practicable, from the sides to the bottom of the dish, and 40 c.c. of strong pure sulphuric acid rapidly poured on. Fumes of hydrochloric and chlorochromic acids are evolved, and completely expelled by applying heat. The temperature is raised until the sulphuric acid begins to fume, thereby ensuring the dehydration of silicic acid. After removal of the flame and cooling for a few minutes, water is cautiously added. To prevent undue corrosion of the nickel vessel, the turbid liquid is transferred to a porcelain dish, and, after making the bulk about ½ litre, boiled for fifteen to thirty minutes, or until the sulphates have completely dissolved. The silica is filtered off, washed thoroughly, ignited in a platinum crucible, and weighed. The silica so obtained should be white, but, as a few m.grms. of metallic oxides usually accompany it, the real weight of SiO_2 (from which the silicon is deduced) is obtained by determining the loss in weight occasioned by evaporation with hydrofluoric acid and one drop of sulphuric acid, followed by strong ignition.

It is advisable to test the purity of the reagents by conducting a blank test.

The results are very concordant and apparently exact. Experiments have shown that 90 to 95 per cent of the chromium can be volatilised by the action of the sulphuric acid; the removal of the chromium prevents the contamination of the silica by basic salts of that metal.

Test experiments, wherein known weights of silica were fused with bichromate and sodium peroxide, and the products submitted to the above treatment, have shown that the process brings practically the whole of the silicon into a weighable form.

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EVOLUTION OF CHEMISTRY IN THE LAST TWENTY YEARS.*

By Dr. A. LADENBURG.

(Concluded from p. 227).

Since the observations of Ste. Claire-Deville, the phenomena of dissociation has been regarded and treated as analogous to those of evaporation. Van 't Hoff now shows that there are reactions which are comparable with the process of fusion, and in which a fixed temperature marks the line of separation between two chemically different conditions. This fixed temperature he designates the transition temperature; and he demonstrates the accuracy of his idea in the cases of the formation of double salts (astrakanite), of the preparation of elements in allotropic modifications (sulphur), and of the splitting of racemic substances (sodium ammonium racemate).

He afterwards treated this subject in a much more detailed manner in an important monograph, "On the Formation and Splitting of Double Salts," in which he explains the theory of the matter, and describes the methods for experimentally determining the transition temperature.

These investigations have found very important applications in relation to the deposition of salts from ocean water, and in explaining the splitting of racemic compounds by Pasteur's methods.

This leads us directly to the subject of stereo-chemistry, which has already been discussed, but which has acquired so much importance of late that I must return to it here.

After the propounding of the theory by van 't Hoff and Le Bel, it was only isolated investigations that were, in the first place, carried out with a view to testing it—such, for example, as the splitting by means of fungi of a series of alcohols, which Le Bel succeeded in doing; and the splitting of synthetic coniine, which was of importance inasmuch as it was the preparation, for the first time, of an active base. The theory was subjected to a systematic examination by Emil Fischer, in carrying out his well-known syntheses in the sugar group.

It is simply astonishing that the theory stood the test of this *experimentum crucis*, and that the sagacity of Fischer enabled him to fix the configurations of the individual hexoses without encountering any contradictions in doing so, especially when we take into consideration the recent experiments of Walden, in accordance with which it is possible, by means of simple chemical reactions, to pass at ordinary temperatures from an active substance to its enantiomorph.

As regards the application of the theory of asymmetric carbon atoms to molecules with doubly linked carbon atoms—a matter that van 't Hoff had already mentioned, but one which had met with less attention—very special notice was called to it by Wislicenus, who, moreover, had himself given the first impulse to stereo-chemical conceptions by his earlier and extended investigations of lactic acid.

The researches of Wislicenus and his pupils have certainly supplied most valuable contributions towards the clearing up of these remarkable cases of isomerism—an end towards which (after the discovery of fumaric and maleic acids) a great many chemists, and even Kekulé himself, had aspired in vain. In this domain, however, there are still many unexplained contradictions, as Michael and Auschütz in particular have shown. On the other hand it must be admitted, that by van 't Hoff's theory an extremely plausible explanation of the products arising from the oxidation of fumaric and of maleic acids is rendered possible.

The applications of the doctrine of asymmetric carbon atoms to substances containing rings are also important and interesting. The first principles were laid down by van 't Hoff; but their significance was only fully recognised when Baeyer published his extended investigations upon hydrogenised aromatic compounds, and, in particular, upon the hydrophthalic acids.

While Baeyer's intention in these investigations was to discover weaknesses in the theory, and even to modify it, his labours led instead to a further confirmation of it. Besides this, the credit is due to him of having advanced the so-called tension theory, which has already proved of service in some cases.

Emphasis must be laid upon the fact that the important consequences which the theory of the asymmetric carbon atom brought forth, gave a spur to the more and more complete application of stereo-chemical considerations. In this connection the numerous researches may be mentioned which deal with the non-occurrence of certain reactions, and explain this on stereo-chemical grounds. Amongst these investigations the best known are those of Victor Meyer on the formation of esters. The asymmetry of the nitrogen atom also falls to be mentioned in this connection.

The researches of Hantzsch and Werner were of fundamental significance with respect to the last-named subject, and they were capable of explaining the isomerism amongst

* Read before the British Association (Section B), Dover Meeting, 1899.

oximes, which was already familiar at that time. Hantzsch afterwards extended the views respecting this matter, and turned them to account in explaining the isomeric hydrazones and diazo-compounds. It is true that it was only geometrical isomerism in the case of nitrogenous organic compounds that was proved by these investigations. Le Bel and Ladenburg endeavoured to prove that asymmetric nitrogen can further produce or influence optical activity. The investigations of both have, however, been attacked, but Ladenburg has been able to establish the accuracy of his results.

Another subject that was much discussed was the significance of racemism, about which a clear understanding only became possible upon the introduction of the conception of the transition temperature, and upon the recognition of the analogy between racemic substances and double salts. The most important method of splitting racemic substances—that by means of optically active substances—remained a standing enigma as long as the existence of partially racemic substances was denied. Every difficulty was removed, however, after Ladenburg had shown that such substances do without doubt exist, and after a transition temperature had been recognised in their case also.

Furthermore, the much debated question as to how a truly racemic substance (inactive by intra-molecular compensation) can be distinguished from the mixture of the active components, may now be looked upon as practically settled.

It is beyond doubt that the founding and development of stereo-chemistry (a name which originated with Victor Meyer) is the most important thing that has been accomplished in organic chemistry during the last two decades. Stereo-chemistry possesses a significance for this period similar to that which the foundation and introduction of the theory of aromatic compounds possessed for the twenty years preceding. There are besides, however, other important investigations in organic chemistry which require to be mentioned.

The systematic and, theoretically, almost completed examination of the sugar group has already been referred to. The uric acid group, which so long resisted elucidation and synthesis, is now completely cleared up, and this is chiefly due to Emil Fischer's synthetical investigations.

The hydrogenised aromatic compounds have likewise been referred to already, but the terpenes have not been mentioned. The latter formerly constituted one of the most confused sections of organic chemistry, whereas Wallach has now succeeded in systematising them by his extended and careful researches. But the most important thing about them, the elucidation of their constitution, is still wanting; for, in spite of some fortunate dashes by Baeyer, which led to the synthesis of substances resembling terpenes, no one has yet succeeded in clearing this up.

The discovery of the iodo-, iodoso-, and iodonium-compounds, for which we are indebted to Willgerodt and to Victor Meyer, is also important, and these compounds supply new knowledge concerning the nature of iodine. The discovery of antipyrine by Knorr was of great importance in medicine, and through it the pyrazol group came to be simultaneously explored.

The preparation of the so-called substantive azo-dyes has become of technical importance; and that of synthetic indigo, according to a method discovered by Heumann, promises to become so.

Great advances have likewise been made in the preparation of artificial perfumes. Vanilline has already been referred to. The manufacture of piperonal (heliotropine), and especially the synthesis of ionone by Tiemann and Krüger, fall to be mentioned in this connection.

This account of the most recent phases in the development of our science must not be concluded, however, without reference being made to the valuable, although unfinished, researches which were carried out under the direction of Friedel, and which aimed at the introduction of a new nomenclature into organic chemistry. Even although it has not yet been possible to extend the system to substances containing rings, still there is much that is good and valuable in the principles that have been advanced.

PHOTO-CRYSTALLISATION.*

By FERDINAND G. WIECHMANN, Ph.D.

(Concluded from p. 227).

Calculation of the Results of Analysis.

LET:—

a = amount of sucrose present.
b = amount of total reducing sugars present.
x = amount of dextrose present.
y = amount of levulose present.
s = the specific rotatory power of sucrose divided by 100.
d = the specific rotatory power of dextrose divided by 100.
l = the specific rotatory power of levulose divided by 100.
p = polarisation observed, expressed in circular degrees.

Then,—

$$(as+xd)-yl=p.$$
$$(as+xd)=p+yl.$$
$$xd=p+yl-as.$$
$$x=\frac{p+yl-as}{d}.$$

Substituting this value of x in the equation—

$$x+y=b,$$

there results—

$$\frac{p+yl-as}{d}+y=b.$$
$$p+yl-as+yd=bd.$$
$$yl+yd=bd-p+as.$$
$$y(l+d)=bd-p+as.$$
$$y=\frac{bd-p+as}{l+d}.$$

As y represents the amount of levulose, y deducted from b will give at once the amount of dextrose. Or, if preferred, the value of x can also easily be calculated independently.

Analytical Results.—The analytical results secured were tabulated and here follow. Table VI. records the analytical data obtained; Table VII. shows the percentage composition of the different specimens as calculated from these data.

TABLE VI.

No. of sample.	Polarisation of a 10 per cent solution at 20° C. in a 200 m.m. tube.	Amount of copper reduced. After inversion. Duplicate determinations.		Average of duplicate determinations.	Before inversion. Duplicate determinations.		Average of duplicate determinations.
1.	−11·7	0·2912	0·2908	0·2910	0·2854	0·2848	0·2851
2.	− 8·2	0·2914	0·2917	0·2915	0·2667	0·2683	0·2675
3.	−10·8	0·2900	0·2908	0·2904	0·2822	0·2826	0·2824
4.	− 4·8	0·2919	0·2941	0·2930	0·2497	0·2508	0·2502
5.	−11·4	0·2931	0·2939	0·2935	0·2837	0·2855	0·2846
6.	+ 9·4	0·3001	0·3009	0·3005	0·1863	0·1852	0·1858
7.	− 8·9	0·2765	0·2800	0·2783	0·2721	0·2710	0·2715
8.	− 6·3	0·2960	0·2968	0·2964	0·2717	0·2708	0·2713
9.	− 1·4	0·2808	0·2806	0·2807	0·2691	0·2695	0·2693
10.	− 4·0	0·2929	0·2939	0·2934	0·2490	0·2510	0·2500
11.	− 9·6	0·2840	0·2846	0·2843	0·2778	0·2788	0·2783
12.	+ 9·8	0·3042	0·3032	0·3037	0·1857	0·1866	0·1861
13.	− 4·4	0·2830	0·2855	0·2842	0·2717	0·2741	0·2729
14.	− 6·5	0·2906	0·2934	0·2920	0·2685	0·2683	0·2684
15.	− 5·8	0·2808	0·2797	0·2803	0·2714	0·2708	0·2711
16.	− 0·2	0·3000	0·2998	0·2999	0·2541	0·2539	0·2540
17.	− 2·9	0·2833	0·2849	0·2841	0·2738	0·2723	0·2731
18.	+ 9·0	0·3033	0·3045	0·3039	0·1871	0·1868	0·1869

* *School of Mines Quarterly*, vol. xvii., No. 4.

TABLE VII.

Number of specimen.	Percentage composition. Sucrose.	Dextrose.	Levulose.	Ratio. Dextrose.	Levulose.
1.	2·04	46·03	49·11	1	1·06
2.	8·17	43 36	45·52	1	1·05
3.	2 74	46·18	48·04	1	1·04
4.	14·53	40·54	42·19	1	1·04
5.	3·03	45·86	49·16	1	1·07
6.	38·39	32·07	28·31	1	0·88
7.	2·27	46·11	44·18	1	0·96
8.	8·58	46·24	43·99	1	0·95
9.	3·85	53·63	35·87	1	0·67
10.	14·71	41·34	41·33	1	1·00
11.	2·10	46·90	45·79	1	0·98
12.	39·44	32·10	28·34	1	0·88
13.	3·91	50·88	39·84	1	0·78
14.	8·11	45·52	43·60	1	0·96
15.	3·15	49·21	40·90	1	0·83
16.	15·70	46·23	37·86	1	0·82
17.	3·79	52·72	38·06	1	0·72
18.	39·21	31·47	29·28	1	0·93

This table exhibits some interesting relations.

The sucrose originally present has been partly transformed into invert sugar. The increase of invert sugar over and above the amount originally present in the solutions can be gathered from the following :—

TABLE VIII.

Specimen number.	Conditions to which specimens were subjected.		Percentage amount of sucrose inverted.
1.	Sunlight	Acid	7·06
2.	,,	Neutral	0·93
3.	,,	Acid	16·66
4.	,,	Neutral	4·87
5.	,,	Acid	38·97
6.	,,	Neutral	3·61
7.	Diffuse daylight	Acid	6 83
8.	,, ,,	Neutral	0·52
9.	,, ,,	Acid	15·55
10.	,, ,,	Neutral	4 69
11.	,, ,,	Acid	39·90
12.	,, ,,	Neutral	2·56
13.	Darkness	Acid	5·19
14.	,,	Neutral	0·99
15.	,,	Acid	16·25
16.	,,	Neutral	3·70
17.	,,	Acid	38·21
18.	,,	Neutral	2·79

Inversion has proceeded very much more rapidly in the acid solutions than in the others. The amount of sucrose inverted in the corresponding members of each of the three series is fairly constant. Thus in—

Specimen number—	Sucrose inverted.
1	7·06
7	6·83
13	5·19
3	16·66
9	15·55
15	16·25
5	38·97
11	39·90
17	38·21

And again—

Specimen.	Sucrose inverted.
2	0·93
8	0·52
14	0·99
4	4·87
10	4·69
16	3·70
6	3·61
12	2·56
18	2·79

These results were to be anticipated and are in perfect accord with the teachings of the ion theory; inversion was more rapid in the acid than in the neutral solutions because the inversion of sucrose is proportional to the number of free hydrogen ions present. The total amount of inversion produced is practically the same in the corresponding members of the different series, because the amount of acid used to produce inversion was the same in all instances.

The last two columns of Table VII. show the ratio which obtains between the dextrose and the levulose of the specimens analysed.

Disregarding series, and considering all of the specimens studied, it will be seen that, in those which were wholly solid when analysed, the dextrose-levulose ratio is as follows :—

Specimen number.	Ratio of Dextrose to Levulose.
1.	1 : 1·06
2.	1 : 1·05
3.	1 : 1·04
4.	1 : 1·04
5.	1 : 1·07
7.	1 : 0·96
10.	1 : 1·00
11.	1 : 0·98
14.	1 : 0·96
Average	1 : 1·018

That is to say, the ratio between the dextrose and the levulose in the crystalline solids is practically one to one.

This is confirmatory of the view generally accepted regarding the composition of invert sugar, the molecular mass of which is expressed by the formula $2C_6H_{12}O_6$.

The existence of invert sugar as a definite crystalline solid would thus seem to be clearly established. In recognition of this fact it appears to the writer that it would be entirely appropriate to designate this substance as *invertose*, a name indicative of the origin of this sugar, and at the same time suggestive of its individuality.

The sucrose found associated with invertose in the specimens studied ranges from 2·04 to 14·71 per cent. These crystalline compounds of sucrose and invertose may perhaps be likened to alloys; that is to say, they may be regarded as mixtures of definite compounds, combined in varying proportions.

CELLULOSE CHEMICALLY MODIFIED.

By S. FERNCEZI.

As far back as the seventeenth century various objects have been made of a mixture composed of paper pulp, gypsum, resin, or some similar substance. After this, paper and cardboard impregnated or covered with substances impervious to moisture, such as resins, wax, asphalte, varnish, &c., have been used for covering walls and roofs. But in every case the vegetable cell, though destroyed, retained its original physiological properties. In this article we propose to deal with products, the preparation of which necessitates the more or less complete destruction of the vegetable cell of the raw material by means of chemical reagents, the final result being an amorphous mass fit for industrial treatment.

I. *Parchment Paper.*—When unsized paper is dipped into sulphuric acid at 30° B., and the excess of acid

eliminated by washing and neutralisation, we obtain parchment paper, a product impervious to water, and resembling true parchment prepared from the skins of animals. The outsides of the cells become softened and unite to form a compact amorphous mass. Several kinds of parchment paper can be produced, this diversity depending on the composition and thickness of the raw material employed.

II. *Temporary Popularity of Parchment Paper.*—Thirty years ago sulphitic cellulose became the most important substance in the manufacture of paper, and it was soon recognised that when saturated for a long time in a pulping machine, it formed a viscous mass from which, from the point of view of transparency and impermeability to water and fatty bodies, a parchment paper could be prepared. It is supposed that here also, as in the case of parchmentised paper, a portion of the finely divided cellulose is transformed into hydrocellulose, but there is nothing to prove that this supposition is correct. As the price of this material is only half that of true parchmentised paper, it has supplanted this latter, and is almost exclusively used for packing perishable articles, such as food stuffs. The very thin, vitreous, transparent varieties are known commercially under the name of "pergamyn," and are used for packing goods of superior quality. To estimate the quality of this paper, above all its impermeability to fatty matter, recourse is had to what is called the "blister" test; the paper is held vertically over the flame of a candle, the quality is good if, before the paper commences to burn, a number of small blisters are formed very close to one another. To distinguish the old from modern parchment paper, it is submitted to mastication; the old kind gives a fibrous mass with short fibres; while true parchment paper gives a more or less hard mass, in which the presence of fibres cannot be detected.

III. *Cellulose.*— When the trituration of sulphitic cellulose is carried to an extreme so as to completely destroy the textile fibres, and to transform it into a uniform amorphous pulp, and this pulp is allowed to evaporate spontaneously, we obtain blocks of amorphous cellulose. This product has been named "cellulith;" the operation lasts, according to the nature of the cellulose used, from 40 to 150 hours. The cellulose, in a state of very fine division, entangles a large quantity of air, the presence of which might have a deleterious effect. For this reason it is advisable to remove the air either by means of a jet of steam, or by boiling the cellulose pulp briskly for an hour or two; the colouring matter, soluble or insoluble, should be added before this operation, when a coloured cellulith is desired. Cellulith can be worked like horn, ebonite, and similar substances. This new product is very suitable for the manufacture of valves; it resists the action of alcohol, petroleum, fats and oils, and is fairly elastic.

IV. *Vulcanised Fibre.*—Sulphuric acid of a given concentration is not the only agent which transforms cellulose into an amorphous mass; chloride of zinc and ammoniacal oxide of copper, in concentrated solution, act in the same manner. This property of chloride of zinc has already been put to profitable use since 1878 in the United States, for the manufacture of hard cardboard impervious to water, and for some years a factory has existed in Germany for the fabrication of vulcanised fibre. The manufacture of these products rests on the joining together by pressure of sheets of parchmentised paper, for which chloride of zinc is used in preference to sulphuric acid, since the least trace of any of this latter remaining between the layers would cause destruction of the material. The treatment with chloride of zinc is very difficult and complicated, especially if it is desired to obtain cardboard of 10 m.m. in thickness. Thin unsized paper is dipped in a solution of chloride of zinc of a known strength and at a given temperature. After removing the excess of the reagent the mass obtained is submitted to the action of suitable pressure until it is of the required thickness. It is washed and then exposed for some weeks to the action of the wind and rain; this appears to be an important factor in the conversion of cellulose into hydrocellulose; it seems to be indispensable if great thickness is required of sufficient hardness and durability; it is then washed a second time. Commercially two kinds of vulcanised fibre are known, the flexible and the hard. The first can be very advantageously used in the manufacture of valves, pipes for the conduct of acids, alkalis, and gases; in a word, it can be used to replace indiarubber and leather. The hard modification is made not only in the form of sheets, but also in tubes, rods, &c.; and it can be sawed, turned, polished, &c., and is manufactured either in red, grey, or black, and is one of the worst conductors of electricity. For some time past vulcanised fibre has been used for the manufacture of cogged wheels; they run very smoothly and without noise.

V. *Celluloid.*—The treatment of cellulose by a mixture of concentrated sulphuric acid and fuming nitric acid gives rise to the formation of nitrocellulose, which is the starting point for the higher explosives; we shall not here, however, treat of this question. Another application of nitrocellulose is worthy of attention, that is its use in the manufacture of celluloid, a body which lends itself to the most varied uses. According to the method adopted by Hyat Brothers, the acid mixture falls in small drops on to a sheet of paper, which is slowly unrolled; this sheet is washed until all trace of acid has disappeared, is dried, cut up, and ground, and then intimately mixed with camphor. The plates thus prepared begin to soften at 80°, and at 125° they become plastic and malleable, so that they can be given any desired form. When heated to 190°, celluloid loses its transparency, and at a higher temperature it decomposes, giving off a reddish smoke. Although the addition of camphor has diminished the explosive force of the mixture, celluloid is nevertheless extremely inflammable, and contact with a match is sufficient to cause a mild form of explosion. Celluloid is capable of most varied applications.

VI. *Pegamoid.*—A few years ago English manufacturers placed on the market articles imitating leather made from cotton and paper. These articles were waterproof, and could be given any desired colour. They were called pegamoid. The surface of pegamoid is covered with a material the composition of which is kept secret, but it is supposed to consist of celluloid made pasty, probably by the addition of some oil. All articles made of pegamoid have a smell of camphor, which confirms the presence of celluloid. Among the principal applications of pegamoid we may mention tents, trunks, portmanteaus, curtains, &c. Pegamoid tissue can be pressed better than leather; it costs less and lasts longer. Pegamoid paper is not affected by grease, so cannot be printed by means of any oily inks, unless first treated with a certain quantity of siccative and salts. As the sun and rain have no action on pegamoid it can be used for permanent advertisements and for other outdoor purposes.—*Zeitschrift fur Angewandte Chemie*, 1899, p. 51.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

The following are the abstracts of papers received during the vacation, and published in the *Transactions*:—

106. "*Researches on the Alkyl-substituted Succinic Acids.* Part I. *Methods of Preparation.*" By William A. Bone and Charles H. G. Sprankling.

These acids may be prepared in quantity from the ethyl cyano-succinates produced by the interaction of ethyl cyanacetate and the esters of α-brom-fatty acids (*Proc.*, 1899, xv., 5).

An account is given of the properties of the ethyl

methylcyanosuccinates, the corresponding methylsuccinic acids, their characteristic anhydrides, anilic acids, and calcium salts.

107. "*Some Derivatives of Dibenzyl Ketone.*" By Francis E. Francis, B.Sc., Ph.D.

Following R. Schiff's work on the interaction of benzal-aniline and acetoacetic ester and similar ketones, three isomeric addition products were obtained when dibenzyl ketone was employed. The first is produced by the action of corresponding amounts of the ketone and benzal-aniline, the second when the reaction takes place in the presence of traces of piperidine, and the third by the action of a trace of sodium ethoxide on either of the addition compounds obtained in the preceding reactions. No colour reaction with ferric chloride is given by either the ketone or any of the three isomeric substances. Like dibenzyl ketone, desoxybenzoin when treated with benzal-aniline gives three substances corresponding to the above, but, unlike it, it gives a fourth with piperidine, which is much less soluble and possesses a much higher melting-point than the others. The oxime and hydrazone, and the compounds formed by the action of ammonia and aniline on monobromodibenzyl ketone, are described.

108. "*Action of Light and of Oxygen on Dibenzyl Ketone.*" By Emily C. Fortey, B.Sc.

When dibenzyl ketone is exposed to air in presence of sunlight, partial decomposition takes place with formation of benzaldehyde, benzoic acid, and phenylacetic acid. After prolonged exposure of a sealed tube containing the ketone with oxygen, another reaction was found to have taken place, carbon monoxide and toluene being produced, together with a substance melting at 193—194°, and having a composition corresponding with the formula $C_{15}H_{13}O$. These products were also formed when dibenzyl ketone was exposed in vacuous tubes or tubes filled with carbon dioxide.

109. "*The Vapour Pressures, Specific Volumes, and Critical Constants of Hexamethylene.*" By Sydney Young, D.Sc., F.R.S., and Emily C. Fortey, B.Sc.

A specimen of hexamethylene obtained by fractional distillation from Galician petroleum was found to solidify, though not completely, in an ordinary freezing mixture. It was therefore still further purified by fractional crystallisation until the melting-point rose to 4·7°. The density of the liquid at 0°/4° was 0·79675, b.-p. 80·9°, at 760 m.m. The vapour pressures, specific volumes, and critical constants were determined; the latter are:—Critical temperature = 280·0°, critical pressure = 30252 m.m., critical volume of a grm. = 3·659.

110. "*The Composition and Tensions of Dissociation of the Ammoniacal Chlorides of Cadmium.*" By Wm. R. Lang, D.Sc., and Albert Rigaut.

This paper gives the results of experiments on the compounds formed by cadmium chloride with ammonia. The compound formed by the action of liquid ammonia at a temperature of −70° has the formula $CdCl_2,6NH_3$. This substance, heated to 100°, loses ammonia, becoming $CdCl_2,2NH_3$, which is extremely stable, like the corresponding salt of zinc, and begins to decompose at 210°, whilst at 300° decomposition is still incomplete, By the action of a solution of ammonia the diammoniacal compound is always obtained; if the hexammoniacal and those intermediate are required, gaseous ammonia must be passed into the solution. The tensions of these compounds, at temperatures varying from 0° to 70°, were measured; they show that at 60° the hexammoniacal compound ceases to exist, and, consequently, for the possible penta-, tetra-, and tri-ammoniacal compounds, temperatures between 60° and 100° must be employed.

111. "*The Aluminium-mercury Couple.* I. *Action of Sulphur Chloride on some Hydrocarbons in presence of the Couple.*" By Julius B. Cohen and Frederick W. Skirrow.

It has been shown by Hirst and Cohen (*Trans.*, 1895, lxvii., 826) that the action of the aluminium-mercury couple closely resembles that of aluminium chloride (Friedel and Crafts, *Ann. Chim. Phys.*, 1884, [vi.], i., 520). The authors find that the couple is capable of wide application both as a condensing agent and as a halogen carrier. Sulphur chloride (S_2Cl_2) acts vigorously on the aromatic hydrocarbons in presence of the couple forming the disulphides. *Diphenylene disulphide*, $C_6H_4{:}S_2{:}C_6H_4$, and *ditoluylene disulphide*, $C_7H_6{:}S_2{:}C_7H_6$, were prepared in this way.

Dixylylene disulphide yields, on distillation, xylyl hydrosulphide, a liquid with a low boiling-point. The corresponding cumene compound forms a crystalline sulphydrate, $C_9H_{11}SH$, m.p. 87—90°. A compound probably identical with this is obtained from pseudocumylene disulphide together with the sulphide, $(C_9H_{11})_2S$, m.p. 110—111°. The products obtained by the distillation of dicymylene disulphide are liquid, and consist of a mixture of the sulphide and hydrosulphide. Sulphur chloride also acts on heptane in presence of the couple; but the product could not be crystallised.

112. "*The Aluminium-mercury Couple.* II. *The Action of Bromine on Organic Compounds in presence of the Couple.*" By Julius B. Cohen and Henry D. Dakin.

The aluminium-mercury couple may be used as a bromine carrier. In presence of small quantities of the couple, bromine forms substitution products with the aromatic hydrocarbons and with the paraffins, very satisfactory yields being obtained. The following substances were prepared in this way:—Bromobenzene, C_6H_5Br; bromotoluene, C_6H_4MeBr; bromo-*m*-xylene, $C_6H_3Me_2Br$; chlorobromobenzene, C_6H_4ClBr, from chlorobenzene; bromo-*p*-chlorotoluene, $C_6H_3MeClBr$, from *p*-chlorotoluene; *p*-dibromobenzene, $C_6H_4Br_2$, from bromobenzene; 1:2:4:5-tetrabromobenzene, $C_6H_2Br_4$, and hexabromobenzene, C_6Br_6, from dibromobenzene; and dibromochlorotoluene, $C_6H_2MeClBr_2$, from bromo-*p*-chlorotoluene. Heptyl bromide, tetrabromoheptane, $C_7H_{12}Br_4$, and a third product, isomeric or polymeric with the latter, were obtained from heptane.

113. "*Experiments on the Constitution of Isocamphoronic Acid.*" By W. H. Perkin, jun., and Jocelyn Field Thorpe.

During the course of experiments on the synthesis of isocamphoronic acid, the authors have prepared a substance of the constitution $CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, which Baeyer suggested as probably representing this acid, but they find that their synthetical acid is not identical with isocamphoronic acid.

When the sodium derivative of ethyl cyanodimethylglutarate, $CO_2Et{\cdot}C(CN)Na{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2Et$ (compare *Trans.*, 1899, lxxv., 63), is digested with ethyl bromacetate, *ethyl cyanodimethylbutanetricarboxylate*,—

$$\begin{matrix} CO_2Et{\cdot}C(CN){\cdot}CMe_2{\cdot}CH_2 \\ | \qquad\qquad | \\ CH_2{\cdot}CO_2Et \quad CO_2Et \end{matrix},$$

is obtained as a colourless oil which boils at 223—227° under 25 m.m. pressure. This ethereal salt, on hydrolysis with sulphuric acid, yields the *dimethylbutanetricarboxylic acid*, $CO_2H{\cdot}CH_2{\cdot}CMe{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, represented above.

This acid has the very remarkable property of being apparently incapable of crystallising, as even when prepared by the hydrolysis of its pure ethyl salt—a colourless oil boiling quite constantly at 182—183° (22 m.m.)—or when set free from its characteristic calcium salt, it is always obtained as a thick colourless syrup. It thus differs widely from isocamphoronic acid, which crystallises with great facility.

When dimethylbutanetricarboxylic acid is distilled, it is converted into the corresponding *anhydro-acid*,—

$$\begin{matrix} CH_2{-}CH{\cdot}CMe_2{\cdot}CH_2 \\ | \quad | \qquad | \\ CO{\cdot}O{\cdot}CO \qquad CO_2H \end{matrix},$$

a colourless oil which distils at 240—242° under 16 m.m. pressure.

114. "*The Cis- and Trans-β-phenylbutane-aa₁a₂-tricarboxylic Acids.*" By JOCELYN FIELD THORPE and WILLIAM UDALL.

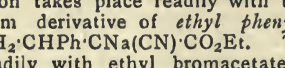
These acids, which are constituted somewhat analogously to the dimethylbutanetricarboxylic acid described in the preceding abstract, may be prepared as follows:—

In the first place, ethyl cinnamate is digested with the sodium derivative of ethyl cyanacetate, when combination takes place readily with the formation of the sodium derivative of *ethyl phenylcyanoglutarate*, $CO_2Et{\cdot}CH_2{\cdot}CHPh{\cdot}CNa(CN){\cdot}CO_2Et$. This compound reacts readily with ethyl bromacetate, yielding *ethyl phenylcyanobutanetricarboxylate*,—

$$CO_2Et{\cdot}CH_2{\cdot}CHPh{\cdot}C(CN)(CO_2Et){\cdot}CH_2{\cdot}CO_2Et.$$

This ethereal salt, which is a thick oil boiling at 270—280° (20 m.m.), is converted on hydrolysis into a mixture of the cis- and trans-*phenylbutanetricarboxylic acids*, $CO_2H{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$. The *trans*-acid crystallises from water in prisms containing $\frac{1}{2}H_2O$, but in the anhydrous condition it is a gum, with properties somewhat similar to those of the dimethylbutanetricarboxylic acid above described. The *cis*-acid melts at 178—180°, and is much more soluble in water than the *trans*-acid.

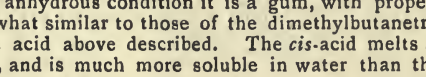
When treated with acetyl chloride, both acids yield the same anhydro-acid of the probable constitution—



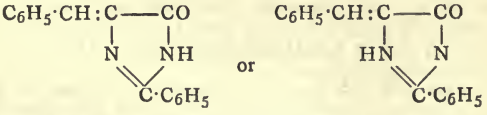
which melts at 134—135°.

115. "*Further Studies on the Acids of the Acetylene Series.*" By SIEGFRIED RUHEMANN and ALFRED V. CUNNINGTON.

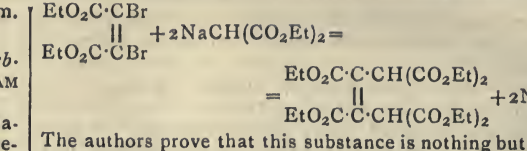
Ruhemann and Browning (*Trans.*, 1898, lxxiii., 723) have shown that the ethyl salts of unsaturated acids combine with piperidine, and that, in the case of ethyl phenylpropiolate, union takes place with great evolution of heat, Diethylamine does not combine with the salt until the mixture is heated to 100°, though like piperidine, it combines with ethylacetylenedicarboxylate very readily at ordinary temperatures. The compounds thus formed have the general formulæ—



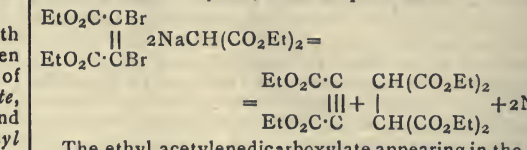
The authors further show that whilst urea and hydroxylamine react with ethyl phenylpropiolate, forming the ureide, $C_6H_5{\cdot}C{:}C{\cdot}CONHCONH_2$ (pale yellow needles, m. p. 220°), and the hydroxamic acid, $C_6H_5{\cdot}C{:}C{\cdot}C(NOH)OH$ (colourless needles, m. p. 168—169°) respectively, benzamidine produces a cyclic compound (yellow needles, m. p. 274°), either—



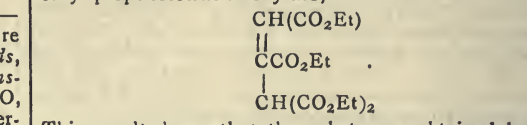
benzal-phenylglyoxalidone. They have also studied the additive products obtained by the action of bromine on ethyl phenylpropiolate and ethyl acetylenedicarboxylate (*i.e.*, ethyl dibromocinnamate and ethyl dibromomaleate respectively), and point out the remarkable difference in their stability. Ethyl sodiomalonate does hot react with ethyl dibromocinnamate, but it does with ethyl dibromomaleate. This action, however, does not occur in the manner stated by G. Pum (*Monats.*, 1888, ix., 446), who supposed that ethyl dimalonylmaleate was formed according to the equation—



The authors prove that this substance is nothing but ethyl ethanetetracarboxylate, which is produced thus:—



The ethyl acetylenedicarboxylate appearing in the equation unites with the ethyl malonate present and forms ethyl propenetetracarboxylate,—



This result shows that the substances obtained by Pum from his so-called ethyl dimalonylmaleate are the well-known products of the transformation of ethyl ethanetetracarboxylate. His dimalonylmaleic acid is ethenyltricarboxylic acid, and his diglycolylmaleic acid appears, therefore, to be succinic acid.

116. "*A Contribution to the Chemistry of the Mandelic Acids.*" By ALEX. MCKENZIE, M.A., D.Sc.

The work was undertaken in order to obtain *d*- and *l*-mandelic acids for the preparation of the optically active phenylalkyloxyacetic acids recently described by the author (*Trans.*, 1899, lxxv., 753). Although recourse was eventually had to amygdalin as a convenient source of *l*-mandelic acid, the results with mandelic acid are given in view of the attention at present directed to the general subject.

Inactive mandelic acid was resolved on a large scale by use of quinidine and cinchonine. From the pure *d*- and *l*-acids so obtained, the salts of cinchonine, cinchonidine, quinine, quinidine, strychnine, brucine, and morphine were prepared, solubility determinations of which showed that the acid can be conveniently resolved into its optically active components by quinine, or, better, by morphine in alcoholic solution.

A number of metallic salts of the mandelic acids were prepared with the view of ascertaining whether any of them would lend themselves to separation by crystallisation. The attempts to obtain the separation of one enantiomorph by spontaneous crystallisations were unsuccessful, owing, the author supposes, to the "transition temperature" not having been reached, or to hemihedrism being absent or masked in the crystals of the active isomers.

117. "*Non-existence of the so-called 'Suboxide of Phosphorus.'*" By DAVID LEONARD CHAPMAN and F. AUSTIN LIDBURY.

The authors have examined specimens of the supposed suboxide, prepared by the methods of Goldschmidt and Reinitzer, and of Michaelis and Pitsch, and have compared their physical and chemical properties with those of red phosphorus in a finely divided state, prepared by the action of sunlight on a strong solution of phosphorus in carbon disulphide. They find complete coincidence of properties in both cases; and it is pointed out that no physical or chemical property has yet been observed by which these substances may be distinguished from one another. Analyses show that when purified as completely as possible, the percentage of phosphorus is greater in all cases than the formula P_4O demands; the impurities in the phosphorus being due chiefly to the presence of acids of phosphorus formed by the action of water during preparation.

They conclude that the so-called suboxide is only an impure form of red phosphorus.

118. "*The Chlorine Derivatives of Pyridine.* Part III. *The Interaction of Chlorine and Pyridine Hydrochloride.*" By W. J. Sell, M.A., F.I.C., and F. W. Dootson, M.A.

The authors have previously described a method of obtaining a considerable number of the chloropyridines (*Trans.*, 1898, lxiii., 432). With a view to simplifying the method of increasing the yield, they have examined the action of chlorine on pyridine hydrochloride, and succeeded in obtaining (1) a dichloropyridine not hitherto obtained by them, (2) a tetrachloropyridine, in large quantity, melting at 21—22°, (3) pentachloropyridine, (4) an aminotrichloropyridine, and (5) a compound of the empirical formula $C_{10}Cl_{11}HN_2$ and certain of its derivatives.

The substance (5), which is formed in considerable quantity, is regarded as being derived from two pyridine nuclei, and is still under examination.

119. "*Amidoamidines of the Naphthalene Series.*" By Raphael Meldola and Percy P. Phillips.

The authors have continued the investigation of the ethenyltriamido-naphthalene described in 1887 (Meldola and F. W. Streatfeild, *Trans.*, li., 691). The acetyl and benzoyl derivatives are described, and the acid character of the NH-group of the amidine ring is made known by the formation of a silver compound and the corresponding N-methyl derivative. The diazotisable character of the NH_2-group has been further studied, and it is shown that the amidoamine is also capable of combining with diazonium salts of other bases. The products do not appear to be simply diazoamido- or amido-azo-compounds as might have been expected from their mode of formation. The investigation of the latter is being continued.

PHYSICAL SOCIETY.

Ordinary Meeting, November 18th, 1899.

Prof. Lodge, F.R.S., President, in the Chair.

By invitation of Prof. Ayrton, this meeting was held in the Physical Laboratory of the Central Technical College.

Mr. F. S. Spiers read a paper on "*Contact Electricity.*" The object of the paper was to determine in a more satisfactory manner than has hitherto been attempted the part played by the medium in the potential difference which arises when two dissimilar metals are put in contact. The first experiments were made with a piece of apparatus used by Professors Ayrton and Perry about twenty years ago. This apparatus, in which the metals in contact are capable of a rotation of 180° about a vertical axis, and are placed between two vertical inductors connected to a quadrant electrometer, was afterwards considerably improved, and the compensation arrangement of Lord Kelvin was introduced so as to measure the potential differences by a null method.

The metals first used were platinum and zinc, but, on account of the low melting-point of the latter metal, it was replaced by aluminium.

In order to try and remove the air sheets which cling to the surfaces of the metals, the tube was repeatedly heated and exhausted. The potential difference between the plates was found to gradually fall as this was done. It was proved that this was due to the oxidation of the aluminium, for, on cleaning its surface, the original effect was again obtained. Attempts were then made to remove the oxygen by displacing it with hydrogen; but, after four washings with pure dry gas and at low pressures, there was still enough oxygen left to completely oxidise the aluminium. The oxide of aluminium is not decomposed by hydrogen at a bright red heat. It was therefore decided to substitute iron and burn out the oxygen with hydrogen by encasing the lower part of the apparatus in a copper tube and heating to bright redness with a blowpipe flame. By this means the value of the Volta effect between iron and platinum in an atmosphere of hydrogen was found to be 0·6 of a volt, the platinum being positive to the iron. This result is different both in magnitude and sign to that obtained when air is the medium.

The Chairman said he had given the subject of contact electricity some attention during the last fifteen years, and the author had performed a valuable series of experiments, which he should have liked to have seen done several years ago. He had always felt that a vacuum would never get rid of the condensed air films. The burning out process used had provided the most reliable results upon the subject.

Dr. Lehfeldt pointed out that the action of hydrogen upon ferric oxide was a limited one, and that it was impossible to bring about complete deoxidisation in that manner. At a dull red heat the ratio between the water-vapour and oxygen present is about 20 to 1.

Prof. Perry expressed his interest in the experiments, but said that they had not affected his opinion upon the nature of the Volta effect.

Prof. Armstrong said he was not wholly satisfied with the results, although a substantial approach to a solution had been made. The author had fully realised the difficulties of the experiments, but he had treated the matter as a surface gas effect, and had not guarded against moisture. Gases must be both dirty and moist before chemical action can take place, and we cannot expect to arrive at a solution of the problem until we have removed not only oxygen, but dirt and moisture. It is impossible to completely exhaust the apparatus, and a number of molecules must always be left which is more than necessary to produce the Volta effect; moisture can never be got rid of by exhaustion. The method of Dewar, of using liquid oxygen or liquid hydrogen would get rid of gases and water-vapour, and in this manner it would be possible to perform experiments which could be regarded as final. If the effect disappeared at low temperatures, it might be urged that the temperature was too low for it to be produced. The author must have been dealing with combination effects, for it had been proved that hydrogen alloyed both with platinum and iron at a dull red heat.

Mr. Cooper said he would like to see the experiments repeated after precautions had been taken to remove nitrogen from the apparatus.

Prof. S. P. Thompson said he had recently taken part in a discussion upon the subject with some earnest followers of the old contact theory. They uphold that the property of metals which determines the potential difference when two are put in contact is as fixed and definite as other physical properties, such as density; and that the potential difference observed in air is approximately the same as the true potential difference. It has been agreed to call the former the apparent potential difference. Prof. Thompson said that, according to Pellat, the real Volta effect was near to the effect observed in air. In circuits formed of metals there are other electromotive forces of the order of a millionth of a volt. The chemical electromotive forces in a circuit are of the order of a volt. The value of the Volta effect derived from thermodynamical considerations concerning the Peltier effect, is much smaller than observed chemical potential differences. If, however, we take into account, not only the Peltier effect, but also the Thomson effect, we will have other terms entering into the equations, which may tend to give a value more nearly equal to a volt. Prof. Thompson said that, in observing chemical E.M.F.'s, the Peltier effects did not come into the question, because of their smallness compared with the value of the chemical effect.

Prof. Perry pointed out that the Peltier effect was not distinct from the Volta effect, but was simply the differential coefficient of it.

The Chairman said that if a circuit containing Peltier effects were treated thermodynamically, as if it were a

reversible heat engine, we could arrive at an equation connecting the value of the Peltier effects with the rate of change of the whole electromotive force in the circuit with temperature. The electromotive force which changed was not necessarily the Volta effect.

Prof. Perry said he thought it was.

Prof. Ayrton suggested that an advance might be made in the theoretical side of the question if the Chairman were to put in writing his objections to the statement that the E.M.F. concerned was the true Volta effect. The extent of the Peltier effect proves the variation of the Volta effect with temperature; but because it is small it does not necessarily follow that the Volta effect is small. Where the Volta effect is a maximum or a minimum, the Peltier effect vanishes. The experimental work of the paper did not go far enough to convince him of the nature of contact electricity. Before we can hope to prove anything with respect to the two theories, we must be able to get a cyclic change of events; that is to say, we must be able to change our surfaces and media in a perfectly definite manner, so as to be able at any time to return to the particular state from which we started.

Prof. Everett said that as the variation in the potential difference between two metals in a medium was probably due to slow chemical action, which caused the metals to become less and less susceptible, he should expect that changing backwards and forwards from one medium to another would give to the potential difference an oscillatory variation, gradually becoming smaller and smaller.

The Chairman said he would like to see experiments showing a cyclic effect similar to that mentioned by Prof. Ayrton. The difficulty in these experiments is to avoid chemical action. Chemical action is not necessary to get the Volta effect. The effect would be greatest in dry gas; moisture tends to reduce the effect, and that is why its presence is unimportant.

Prof. Callendar expressed his interest in the surface character of the effect, and its independence of the manner in which the plates were touched.

Dr. Stansfield suggested gold as a suitable metal to be experimented on, because of its non-oxidisability.

Mr. Spiers, in replying, referred to Dr. Lehfeldt's assertion that the whole of the oxygen cannot be removed by hydrogen. In his experiments, however, there was very little ferric oxide and a large quantity of hydrogen, and although it was possible that all the oxide was not reduced, still a large portion of it was. The experiments were to be carried on, and attempts would be made to get a cyclic effect.

A paper on "The Heat of Formation of Alloys" was postponed until the next meeting.

CORRESPONDENCE.

DETERMINATION OF CARBON IN IRON AND STEEL WITHOUT ABSORPTION APPARATUS.

To the Editor of the Chemical News.

Sir,—I beg space in order to make some explanations necessitated by the criticism of H. Brearley (Chemical News, lxxx., 146) on my processes for the determination of "Graphitic and Combined Carbon in Iron" (*Iron Age*, May 11, 1899; Chem. News, lxxx., 121). In the first place, my title for the paper referred to ("Determination of Carbon in Iron and Steel without Combustion Apparatus") would have been more exactly and clearly stated if "Absorption" had been substituted for the word "Combustion."

I did not claim novelty for all the details of the processes; it would be well nigh impossible for any one to present a new process that is novel from end to end. Though some of the details given are decidedly new as applied to the estimation of carbon, novelty is not what I was after. Until my article had been published, I had had no knowledge of any other chemist's previous investigations on the nature of the carbonaceous compound as deposited in copper solution, nor of their essays to make a direct determination of carbon on more or less similar lines of procedure; even since then, I fail to see that my processes have been wholly or largely anticipated, at least not to the extent of ensuring correct results.

The alleged differences beween my figure for carbon (67·5) in the carbonaceous compound, and those decided on by the other investigators (70·96 by Schützenberger and Bourgeois, who described its composition as $C_{11}H_6O_3$; 72·7 by Zaboudsky, who wrote his formula $C_{12}H_6O_3$; and "about 70" by Blair in his book) are not so serious as they may seem to be, but, on the contrary, are small enough, since the carbon compounds experimented on were all prepared and obtained under more or less differing circumstances, and therefore were not exactly similar in composition. These variations would look insignificant when we remember what, in the early days of steel chemistry, were offered as the percentage of phosphorus in the dried phospho-molybdate precipitate; yet we to-day have a very accurate method of phosphorus determination by direct weighing of that precipitate. If Blair's formula for the carbonaceous residue was correctly quoted by my critic to be $(C_{50}H_{21}ClO_{15})_3+O_2$, the percentage of carbon in it should be computed at 65·8 instead of "about 70," and this comes considerably within hailing distance of my figure. It is creditable to Mr. Brearley to have been able to dig up those prior investigations by the other chemists with their formulæ given. I feel sincerely obliged to him for the light of history that has been thrown on the matter, and also because the result of it has practically sustained my position. The factor of 67·5 is not theoretical, but actual, having been standardised by three standard steels of different grades of carbon which have been carefully determined by the regular combustion process. If the carbonaceous compound were soluble in warm dilute nitric acid, as claimed by some, how is it that the factor is only 67·5 instead of much higher, in order to compensate for the alleged loss? It is most important to eliminate copper sulphide and phosphide, which are most usually present in too appreciable quantity in the residue; this is accomplished by washing with warm nitric acid of the dilution recommended. Another requisite to the use of this factor with safety is to stir constantly, or very frequently, while dissolving drillings in copper solution. Never let the work of dissolving be interrupted overnight; else the black precipitate will be apt to have an irregular composition, as my experience has shown. It may be well stated that the golden rule to obtain success in all standardised processes of analysis is to operate under uniformly similar circumstances and conditions. This factor (67·5) applies to pig-iron and steel only; for ferromanganese, for instance, would require a much higher figure, about 80 or 90, depending on mode of operation, acidity, &c., as already announced in my previous paper.

The standard combustion method has a multitude of sources of error to be guarded against; indeed, eternal vigilance is the price of reliable determinations by that method. Dr. Dudley and others have put much stress on the difficulty of weighing correctly, or under exactly similar conditions, the absorption bulbs before and after the combustion, especially in damp weather. This is not surprising, seeing that the absorption apparatus is a bulky affair, and has an enormous amount of surface for the surrounding atmosphere to affect. It is not usually safe to weigh the apparatus until it has been in the balance case about half an hour, or, according to the opinion of the then head chemist of a large steel company in the city, not less than one hour. Some chemists have got so disgusted with this annoyance that they prefer to absorb the CO_2 in barium hydrate and weigh or titrate excess of

alkali. Arnold, in his "Steel Works Analysis," gives an instance of undue increase of weight of his bulbs by the absorption of SO_3 from the high sulphur contents of the carbon residue. Blair asserts that the dehydrating or dechlorinating power of anhydrous copper sulphate deteriorates rapidly, and it must be replaced after every two or three combustions if I remember aright. Langley advises that certain chlorine compounds, sure to be evolved during the combustion, be arrested by sodium oxalate or pyrogallate; Dudley uses a roll of metallic silver and acid ferrous sulphate to catch chlorine,, and silver sulphate to take down HCl and chlorine compounds. The latter chemist also has an auxiliary furnace to pre-heat his oxygen gas, because it is often impure as bought in the market. Auchy demonstrated that potash solution of the usual density, 1·27 sp. gr., did not absorb CO_2 as completely as that of 1·41 sp. gr. would. Frequently has the claim been made with some plausibility that the platinum tube is permeable to gases at a red heat. Still, "there are others" to enumerate.

It may not be out of place here to call attention to the results of the considerable number of analyses made by different chemists in the States recently, on drillings from the same piece of iron. I shall give only results for combined carbon, seven determinations by colour, eight by oxidation with sulphuric and chromic acids, eight by combustion in Pt tube and weighing KHO bulbs, and two by combustion in Pt tube absorbing CO_2 in baryta and igniting and weighing, tabulated as follows :—

		By combustion in a Pt tube.	
By colour.	By oxidation with H_2SO_4 and CrO_3.	Weigh KHO bulbs.	Absorb CO_2 in Ba hydrate. Ignite and weigh.
0·38	0·43*	0·56	—
0·45	0·44	0·91	—
0·52	0·51*	0·36	—
0·48	0·45*	0·52	—
0·35	0·47	0·57	—
0·40	0·45*	0·29	—
0·41	0·45	0·40	0·56
—	0·46	0·35	0·62
Av. 0·43	Av. 0·46	Av. 0·49	Av. 0·59

* By one and the same party.

The foregoing results by dry combustion do not by any means reflect credit on this standard method, though performed by supposedly past masters in their profession, even after making due allowance for accidental errors or irregularites in the sample, both of which are bound to occur occasionally. This table, it will be noted, gives considerable food for serious reflection. I have since received a small sample of that particlar iron, and obtained 0·41 per cent combined carbon by colour, and 0·44 per cent by my process after dissolving in the cold, and 0·48 per cent after dissolving at a gentle heat. In my method 1 grm. of material is taken, whereas in the usual combustion or oxidation processes at least 3 or 5 grms. are required in order to minimise incidental errors by division (and frequently do not).

I am still of the opinion that the method I described for graphite also leaves very little to be desired for simplicity, rapidity, and accuracy, and is really to be preferred over any of the absorption processes in a great majority of cases; it is applicable in all cases where the metal is decomposable by dilute nitric acid. The proof of the pudding is in the eating.

The Gooch crucible, which is the essential part of both my processes, may be cheapened considerably by having it of porcelain with open bottom for a perforated platinum disc, and jacketed with thin platinum foil in lieu of the usual platinum cap for use in ignitions.—I am, &c.,

GEORGE T. DOUGHERTY.

Laboratory of the Sargent Company,
Chicago, U.S.A. Oct. 25, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 17, October 23, 1899.

Simultaneous Phenomena of Oxidation and Hydration under the Combined Influence of Free Oxygen and Light. — M. Berthelot. — The author previously investigated the relation between certain oxidising reactions and certain hydrating reactions. Certain oxidations take place under the simultaneous influence of oxygen and light. The present research investigates further to discover whether, acting on ethylic ether—one of the most simple types of compounds split up by hydration—this substance is susceptible at the same time of hydration; that is to say, changing a portion of itself into alcohol, and at the same time oxidising another portion.

Determination of the Coefficient of Solubility of Liquids.—A. Aignan and E. Dugas.—The authors have already determined this coefficient for two liquids which do not mix in all proportions when the temperature is constant and the liquids do not react upon one another. The present paper contains an account of the determination of the coefficient of solubility of two liquids which do not combine, and where there is a contraction of volume after agitation. The initial conditions of the experiment are as follows :—One of the liquids dissolves in the compound, and the excess of this non-combined liquid dissolves to saturation the compound formed. The determinations were made for aniline and water, and for amylic alcohol and water.

Journal de Pharmacie et de Chimie,
Series 6, Vol. x., No. 1.

Poisoning by Formol.—M. André.—Of late years, owing to the results of bacteriological experiments, formol has gradually come to be used in medicine, and also as a disinfectant. The author describes a case in which a patient took by mistake a spoonful of formol instead of another medicine; formol is a very irritant corrosive poison, and quickly destroys the skin and mucous membrane, besides having a very strong toxic effect. The best and quickest antidote has been found to be spirit of mindererus (acetate of ammonia), which quickly neutralises and decomposes the formol. This treatment, followed by an emetic, was found to be very efficacious, and in two days' time the patient had quite recovered.

Analysis of Gaseous Lemonades.—M. Frehse.—This paper contains the results of a number of analyses of lemonades, all of which were acidulated with tartaric acid; some were sweetened with saccharose and some with glucose. Of thirty-one manufacturers, one used glucose and saccharine together, two replaced a certain quantity of sugar with saccharine, and another added saccharine to increase the flavour of the lemonade.

Action of Dissolved Iodide of Potassium on Mercurous Iodide.—M. François.—Already inserted.

The Estimation of Chlorine, Bromine, and Iodine Mixed.—J. Bougeault.—Already inserted.

No. 2.

Volumetric Estimation of Aniline by Bromine and Bromine by Aniline.—G. Denigès.—Already noticed in this column.

Presence in the Animal Organism of a Soluble Ferment Reducing Nitrates. — E. Abelous and E. Gerard.—The authors show that in most animal organs, though in unequal proportion, there exists a soluble sub-

stance which reduces nitrates. From the facts observed, more particularly under the influence of varying temperatures, it appears probable that this substance is of a diastasic nature.

Clinical Estimation of Urinary Albumenoids.—G. Denigès.—Not suitable for abstraction.

Remarks on the Action of Heat on Pepsine.—V. Harlay.—The author's experiments show that the prolonged action of heat acts in diminishing the activity of the ferment. On the other hand, it is seen that the temperature which destroys pepsine in aqueous solution is about 68°; and at lower temperatures, even at 60°, pepsine undergoes a weakening action. Pepsine, however, appears to be able to resist the action of heat better in simple aqueous solution than in physiological solution; in the latter case the critical temperature is from 55° to 60°.

Detection of Formic Aldehyde in Milk.—Al. Leys.—Although a considerable number of reagents have been proposed for the detection of formic aldehyde, it has frequently happened that, in the case of searching for it in milk, only negative results have been obtained. It is, of course, present in only infinitesimal doses—one five-thousandth being sufficient to preserve milk for one hundred hours at a temperature of 25°. Bisulphite of rosaniline, made according to Schiff's formula, has especially been found to be untrustworthy. One solution only of this class has been found of real practical use by the author; it consists of 1000 c.c. of an aqueous solution of fuchsine at 1/1000th; 10 c.c. of bisulphite of soda at 30° B.; and 10 c.c. of pure concentrated hydrochloric acid. The bisulphite is added to the solution of fuchsine, and when the colour becomes very feeble the acid is added; after a few days the solution becomes perfectly colourless. The test is performed by distilling 100 c.c. of the milk; when about 20 c.c. has come over, a small quantity of this solution is added. If the milk is free from formic aldehyde, the solution remains colourless, even after several days; if, however, only 1/500,000th part of the latter is present, the solution takes an intense reddish violet colour after the lapse of a few minutes; even one-millionth part gives a distinct colouration. A solution of phloroglucine and potash-lye is also a very delicate reagent. If the milk is pure, the solution takes a pale green semi-transparent appearance; if, however, 1/100,000th part of formol is present, a brilliant—though fugitive—salmon-pink colour is produced; the colouration may also be noticed with only 1/1,000,000th part of formol present.

On a Chloro-iodide of Tin.—C. Lenormand.—Already inserted in full.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Arts, 8. (Cantor Lectures). "Enamelling upon Metals," by Henry Hardinge Cunynghame.
Wednesday, 22nd.—Society of Arts, 8. "National Forestry," by D. E. Hutchins.
Thursday, 23rd.—Society of Arts, 4.30. "Old and New Colombo," by John Ferguson.

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NOTICE IS HEREBY GIVEN, that an EXAMINATION for the ASSOCIATESHIP (A.I.C.) and FELLOWSHIP (F.I.C.) of the Institute of Chemistry will be held at 30, BLOOMSBURY SQUARE, London, W.C., on TUESDAY, Jan. 9, 1900, and three following days.

Forms of application can be obtained from the Secretary.

By order of the Council,
J. MILLAR THOMSON, Hon. Registrar.
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Monsieur Joseph Ruet, 7, Rue Saint Claud, Paris.

THE CHEMICAL NEWS.

VOL. LXXX., No. 2087.

A BIBLIOGRAPHY OF STEEL-WORKS ANALYSIS.

By HARRY BREARLEY.

(Continued from p. 234).

MANGANESE (*continued*).

II. SEPARATING OTHER ELEMENTS FROM MANGANESE.

33. *Aluminium.*—ROSE (*C. N.*, ii., 266).—Add $(NH_4)Cl$, boil, add ammonia and boil off excess. Precipitate perfectly free from Mn.

34. *Nickel and Cobalt.*—TERRIEL (*C. N.*, xiii., 133).—Permanganate completely precipitates manganese from ammoniacal solutions.

34*a*. JANNASCH and FRANZEK (*J. I. S. I.*, 1892, i., 493).—Solution of the sulphates converted to double cyanides and Mn precipitated with H_2O_2. Re-precipitation recommended (*J. C. S.*, lxx., ii., 548).

35. *Nickel, Cobalt, and Zinc.*—GIBBS (*C. N.*, xi., 148).—Precipitates in acetic solutions with H_2S.

CLARK (*J. C. S.*, lxiii., 1082).—Soda peroxide precipitates Mn from ammoniacal solutions free from Zn. Re-precipitation is required in order to separate Ni and Co.

TAMM (*C. N.*, xxvi., 37).—Mn is precipitated with $(NH_4)_2CO_3$ free from Ni and Zn.

36. *Zinc.*—JANNASCH and NIEDERHOFHEIM (*C. N.*, lxv., 159).—A mixture of KCN and KHO are added until precipitate is re-dissolved. Mn precipitated with H_2O_2.

36*a*. RENARD (*C. N.*, xx., 35).—Mn precipitated with soda phosphate and ammonia.

36*b*. BAYLEY (*J. C. S.*, liv., 388).—Zn precipitated with H_2S from a solution containing free phosphoric acid.

Separations with H_2O_2.—Mn is separated from a number of elements by adding the mixture to an alkaline solution of H_2O_2; the procedure is very similar in each case. The references are :—

37. *Mercury.*—JANNASCH (*C. N.*, lxxii., 65; and *J. C. S.*, lxviii., ii., 332).

38. *Silver.*—JANNASCH and KAMMERER (*C. N.*, lxxii., 91; and *J. C. S.*, lxviii., ii., 423).

39. *Arsenic.*—JANNASCH and KAMMERER (*J. C. S.*, lxx., ii., 221).

40. *Chromium.*—JANNASCH and CLOEDT (*J. C. S.*, lxx., ii., 222).

41. *Zinc.*—JANNASCH and CLOEDT (*J. C. S.*, lxx., ii., 220 and 546). Also JANNASCH and MACGREGORY (*J. C. S.*, lx., 963).

42. *Copper.*—JANNASCH (*J. C. S.*, lxx., ii., 546).

43. *Copper and Cadmium.*—JANNASCH and ROTTGEN (*J. C. S.*, lxviii., ii., 331).

44. *Tungsten.*—TAGGART and SMITH (*C. N.*, lxxv., 26).—Neither digestion with ammonium sulphide and $(NH_4)Cl$ nor with K_2CO_3 effects a complete separation.

45. *Phosphorus.*—GRANGER (*C. N.*, lxxv., 95).—Fuse with KHO, evaporate acid solution to dryness, re-dissolve, and precipitate with ammonium sulphide.

46. *Chromic Acid.*—BREARLEY (*C. N.*, lxxvii., 131).—Sodium carbonate added *to cold solution*, and filter at once or after heating to boiling-point. Precipitation with soluble phosphate, using considerable excess, in ammoniacal solution.

47. *Copper.*—KNORRE (*J. C. S.*, lii., 530).—To acid solution of sulphates or chlorides add nitroso-β-naphthol in acetic acid. Cu is precipitated.

III. GRAVIMETRIC ESTIMATION OF MANGANESE.

a. As Mangano-manganic Oxide.—

48. EGGERTZ (*C. N.*, xviii., 232).—Precipitate with Br, wash with cold 1 per cent HCl, dry at 100° C., and weigh as hydrated oxide (59·21 per cent Mn), or ignite to Mn_3O_4.

49. KESSLER (*C. N.*, xxvii., 14).—Precipitates with Br and sodium acetate.

50. ABEL (*C. N.*, vi., 125).—Precipitates Mn from ammoniacal solution with bromine.

51. PIESSE (*C. N.*, xxix., 110).—Precipitates with Br and ammonia, and allows to stand eighteen hours.

52. WILLIS (*C. N.*, xxix., 150).—Uses more Br and ammonia, and points out that the precipitation of the Mn is immediately complete.

53. RIGGS (*J. C. S.*, lxii., 536).—Bromine should be added to the hot ammoniacal filtrate.

53*a*. MÜLLER (*J. I. S. I.*, 1886, 392).—Acetate separation of Fe. Precipitates Mn with H_2O_2 and $(NH_4)HO$, and ignites.

54. MEINECKE (*J. I. S. I.*, 1887, i., 469).—ZnO separation of Fe; filtrate mixed with HgO; heat to boiling-point and precipitate with Br. The precipitate is washed with dilute HNO_3 (free from nitrous) and ignited.

55. JUPTNER (*J. I. S. I.*, 1885, 247).—Precipitated sulphide dissolved in acetic acid, evaporated, and ignited to Mn_3O_4.

56. KERN (*C. N.*, xxxii., 100).—Fe and Mn precipitated with KHO, heated in H; mixture powdered under naphtha oil; Fe separated with magnet, and MnO ignited to Mn_3O_4.

57. PARKER (*C. N.*, xxii., 186).—Spiegels contain Cu up to 0·5 per cent; this is precipitated by the Br and ammonia, and to some extent if Mn is precipitated as phosphate.

58. MATHESIUS (*C. N.*, liii., 74).—Oxides of Mn ignited along with NH_4Cl are partly volatilised. (See 17).

59. PICKERING (*C. N.*, xliii., 189).—The degree of oxidation of $MnO_2.MnO$-compounds is influenced by heating in air at 100° C., or even by boiling in water. Compounds variously oxygenated are produced when oxides of manganese are heated to redness in a platinum dish over a Bunsen. Permeability of the platinum probable cause of the error.

60. PATTINSON (*J. C. S.*, lxii., 536).—Mn_3O_4 formed only by ignition at almost white heat, the oxide being protected from reducing agents; heat of a Bunsen not sufficient to form Mn_3O_4; heating over gas blowpipe dangerous, owing to reducing gases permeating the crucible. All ignitions in air need confirmation by a determination of the available oxygen.

61. GORGEU (*J. C. S.*, liv., 653).—After heating to bright redness, Mn_3O_4 absorbs absolutely no oxygen on cooling.

62. MEINECKE (*J. C. S.*, lvi., 311).—To prevent the ignited precipitate containing fixed alkali, it should be heated with $(NH_4)Cl$ and ammonia before filtering.

63. GOOCH and AUSTIN (*C. N.*, lxxvii., 255).—Ignition to Mn_3O_4 may be made in strong Bunsen or blast-lamp in such a way that an oxidising flame covers the entire wall of the crucible.

III.*b. Estimation of Mn as Pyrophosphate.*—

64. GIBBS (*C. N.*, xvii., 195).—Describes the precipitation as ammonium-manganese phosphate. Refers to other metals precipitable as ammonio-phosphates.

65. GOOCH and AUSTIN (*C. N.*, lxxviii., 239).—The success of the precipitation depends mainly on the change of $Mn_3P_2O_8$ to NH_4MnPO_4; the presence of $(NH_4)Cl$ or a substitute essential to completeness

of this change; the proportion $(NH_4)Cl$ to final $Mn_2P_2O_7$ should be at least 50 to 1; large excess not harmful; ammonia used in slight excess; glass vessels available if operation is rapid.

66. McKENNA (*C. N.*, lxiii., 184).—Compares Gibbs's original process (64) and Blair's ("Chem. Anal. of Iron") modification. The precipitate must be quite crystalline; a trace of Mn always found in the filtrate; hot water, $(NH_4)HO$, and $(NH_4)NO_3$ all slightly dissolve the precipitate; glass vessels may be used.

III.*c. Estimation of Mn as Sulphate.*—

67. GOOCH and AUSTIN (*C. N.*, lxxvii., 256).—Estimation as sulphate formerly recognised procedure; definite condition of hydration thought hard to attain to. Volhard used a ring burner in iron casing, and obtained excellent results; authors support crucible on a triangle within a larger crucible, and are able to heat the outer one to redness without risk; good results; regarded as most reliable of the gravimetric processes.

III.*d. Estimation of Mn as Sulphide.*—

68. ROSE (*C. N.*, ii. 302).—Precipitated sulphide not wholly insoluble, especially in liquids containing ammonia salts; the precipitate is deposited slowly.

69. BLUM (*J. I. S I.*, 1890, i., 372).—In presence of Ca the precipitation should be made in boiling solutions and rapidly filtered, as calcium hyposulphite may crystallise out.

70. FRESENIUS (*C. N.*, iv., 150).—Ammonium sulphide does not precipitate very dilute solutions of Mn; $(NH_4)Cl$ favours the precipitation after some time.

71. MEINECKE (*J. C. S.*, liv., 1132).—Precipitated from boiling solutions containing excess of ammonia; a trace remains unprecipitated; large amounts of $(NH_4)Cl$, NaCl, or $NH_4(C_2H_3O_2)$ are without influence. Satisfactorily separates Ca and Mg.

III.*e. Precipitation of Mn as Carbonate.*—

72. FORBES (*C. N.*, xvi., 105).—Precipitates with sodium carbonate.

73. TOSH (*C. N.*, xvi., 168).—Re-dissolves precipitated sulphide in HCl, precipitates with sodium carbonate, and ignites to Mn_3O_4.

74. TAMM (GUYARD) (*C. N.*, xxvi., 37).—Precipitates with ammonium carbonate; claims this, amid much rattle, as a startling discovery. Allen (*C. N.*, xxvi., 81, speaks of it as an old process.

75. AUSTIN (*C. N.*, lxxvii., 242).—Precipitation as carbonate complete; presence of $(NH_4)Cl$ necessary to ensure filterable precipitate. Preferable to weigh as sulphate.

76. GORGEU (*C. N.*, lix., 277).—At the common temperature carbonate or oxide of Mn cannot absorb from air or aërated water a proportion of O greater than corresponds to $MnO_2.MnO$.

III.*f. Estimation of Manganese Electrolytically.*—

77. RICHE (*C. N.*, xxxvi., 90).—Deposited as peroxide. Cu, Ni, Co, Zn, Mg, Al, alkalis or alkaline earths, may be present. Large amounts of Fe injurious.

78. KAEPPEL (*C. N.*, lxxvii., 201; and lxxix., 195).—Deposited partly as metal and partly as MnO_2 from neutral or faintly acid solutions; very strong current used; addition of acetone improves results.

79. VORTMANN (*J. I. S. I.*, 1892, i., 490).—Mn and Hg precipitated simultaneously as an amalgam; Zn, Pb, Cd, Sb, As, and Bi, which do not form coherent deposits, can be similarly estimated (see *C. N.*, lxiv., 227, &c.).

80. ENGELS (*J. C S.*, lxxiv., ii., 52).—Deposited at 80° C. from solutions containing Cr alum, or alcohol and ammonium acetate.

81. BRAND (*J. C S.*, lviii., 294).—After dissolving in pyrophosphate, MnO_2 is deposited, adhering firmly. Ignited to Mn_3O_4.

82. RÜDORFF (*J. C. S.*, lxiv., ii., 94).—Mn should be present as sulphate; deposited hydrated peroxide dried at 60° and weighed.

83. CLASSEN (*J. C. S.*, lxvi., ii., 480).—Solution electrolysed in presence of acetic acid; peroxide ignited to Mn_3O_4.

84. VOLMAN (*J. C. S.*, lxxiv., ii., 50).—Deposited from HNO_3 solution at 50°; small current; solution in oxalate, acetic acid, or pyrophosphate do not give good results.

85. GRÖGER (*J. C. S.*, lxviii., ii., 419. Electro-deposited Mn not entirely peroxide. Only 94 to 96 per cent estimated by KI and thiosulphate, on the assumption that the precipitate is MnO_2.

III.*g. Estimation of Mn (Miscellaneous).*—

86. CARNOT (*C. N.*, lvi., 16).—Precipitated as vanadate from an ammoniacal solution. Ignited precipitate has the composition $2MnO.V_2O_5$.

(To be continued).

NOTES ON A REMARKABLE CASE OF METALLIC CORROSION.

By E. T. ALLEN.

LAST June several boxes of analytical weights, of the make of Bender and Hobein, of Munich, were put away for the summer in an iron safe. The larger weights were of gold-plated brass, the smaller of platinum.

The weights had been in use in the laboratory for one year, and when put into the safe were in good condition. When taken out, after less than three months, the varnished boxes could only be opened by vigorous prising. Moisture had evidently found its way within, for the ivory points of the tweezers, and in some cases the velvet linings of the boxes, were white with mould. The platinum weights were as bright as new, but the top of every one of the gold-plated weights was covered with a white substance which could not be removed by either brushing or rubbing. An examination showed that these weights were abnormally heavy. By careful scraping of more than fifty of them, a small quantity of white powder was obtained, yet sufficient for several satisfactory qualitative tests. It proved insoluble in water, soluble in hydrochloric and nitric acids. The colourless nitric acid solution gave no precipitate with silver nitrate, proving that no halogen was concerned in the corrosion. The hydrochloric acid solution gave no precipitate with ammonia, but a white precipitate with ferrocyanide of potassium. The ammoniacal solution yielded a brownish white precipitate with ammonium sulphide.

Heating on platinum foil revealed the presence of organic matter, though apparently in fragments. On charcoal a white coating was obtained, and this with cobalt nitrate gave the characteristic Rinmann's green. The substance was therefore some compound of zinc—probably either the hydroxide mixed with mould or a zinc salt of some organic acid. Lack of material prevented a more complete examination. Since the weights were tightly boxed, and kept in a closed safe which contained no chemicals of any kind, the action can only be assigned to water and mould, which were certainly present. It is well known that plated metals at exposed points are more susceptible to corrosion than either metal alone, owing to electrolytic action. In such cases it is of course the more positive metal which is attacked. This is seen to be true in the above-mentioned case—the zinc is attacked, while the copper and gold are unaffected. That the brass should be reached through the plating seems remarkable, to say the least. A microscopic examination showed that wherever corrosion had touched the weights, the gold had become granulated or blistered. A case which seems to me to possess some points in common with this has

recently been described by Witter (*Berg. und Hütt. Zeit.*, July 28, 1899, p. 349). The amalgamated plates of a stamp-mill in Smaland, Sweden, were attacked by the water used, which had its source in a peat-bog. The plates became covered with a green slimy substance, which proved to be an organic compound of copper. It is notable that the more positive metal was attacked in spite of the layer of amalgam which protected it, and also that a piece of copper *alone*, after standing six months in the partly evaporated water, was unattacked.

This naturally raises the question, Are gold-plated weights, under ordinary working conditions, preferable to brass weights? Any new light on the subject would be gladly received.

State School of Mines, Rolla, Missouri.

THE DECOMPOSITION OF CARBONIC ACID IN THE PRESENCE OF CARBON.

By O. BOUDOUARD.

In a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 465) I published the results arrived at in my research on the reaction $CO_2+C=2CO$, at a temperature of 650°. I have now continued this research at higher temperatures.

1. *Experiments at* 800°.—I used the same apparatus, with the porcelain tube, described in my preceding paper. The pumice impregnated with metallic oxide was replaced by fragments of carbon of the size of a nut. When the apparatus is filled with carbonic acid gas, the outer tap is closed and the other extremity plunged into mercury. As there will be an increase of pressure on account of the reaction $2CO=CO_2+C$, the gas must be thus allowed to escape freely. The heat is applied for varying periods of time, when the gas is extracted and analysed. I have also made experiments in the presence of charcoal formed by the decomposition of carbonic oxide. The following results were obtained:—

Time.	Wood charcoal.		Retort carbon.		Coke.		Carbon from CO.	
H. M.	CO_2.	CO.	CO_2.	CO.	CO_2.	CO.	CO_2.	CO.
0 8	17·1	82·9	86·7	13·3	83·6	16·4	13·6	86·4
1 0	6·1	93·9	65·8	34·2	—	—	—	—
1 30	—	—	—	—	42·6	57·4	8·0	92·0
2 30	—	—	—	—	—	—	7·1	92·9
6 0	6·7	93·3	—	—	11·0	89·0	—	—
7 0	—	—	43·3	56·7	—	—	—	—
9 0	—	—	—	—	12·8	87·2	—	—
9 30	—	—	29·7	90·3	—	—	—	—

In another series of experiments I used charcoal in much smaller pieces, 2 to 5 m.m. diameter. The results obtained were as follows;—

Time.	Wood charcoal.		Retort carbon.		Coke.	
H. M.	CO_2.	CO.	CO_2.	CO.	CO_2.	CO.
0 8	39·9	60·1	80·1	19·9	79·1	20·3
1 0	9·9	90·1	41·2	58·8	39·8	60·2
1 30	10·1	89·9	—	—	—	—
6 0	6·3	93·7	17·2	82·8	15·6	84·4
9 0	—	—	12·7	87·3	—	—

The results are practically the same with wood charcoal and coke whether large or small fragments are used; with retort carbon there is an increase in the speed of the reaction, but the limit reached with wood charcoal and carbon from CO is not attained—at least, not after being heated for at least nine hours. Considering these figures as a whole, we see that in all the different cases the general phenomena are the same, there is only a difference in the speed of the reaction. The decomposition of the carbonic acid is not complete; but as at 650°, the limit reached at 800° is the same as that obtained in studying the decomposition of carbonic oxide (93 per cent CO and 7 per cent CO_2).

2. *Experiments at* 925°.—Experiments made with the same apparatus as those at 800° show that the quantity of carbonic acid remaining diminishes more and more; the measurements of their volumes becoming more and more difficult, I substituted the ponderable method for the volumetric. For varying periods of time, I passed a current of carbonic acid over carbon. At the escape tap of the apparatus the gaseous mixture was passed through a flask containing baryta-water. A check tube of baryta-water showed that the carbonic acid was completely absorbed. From the weight of carbonate of baryta thus obtained, the quantity of carbonic oxide formed was calculated.

1. 1·25 *Litres of* CO_2 *Gas for Thirty Minutes.*—CO_2BaO obtained = 0·3765 grm.; corresponding CO_2 = 0·0838 grm., or 3·3 per cent (vol.).
2. 3·5 *Litres of* CO_2 *Gas for One Hour Thirty Minutes.*—CO_2BaO obtained = 0·1045 grm.; corresponding CO_2 = 0·3127 grm., or 4·5 per cent (vol.).

At a temperature of 925° there thus still remains in the gaseous mixture resulting from the reaction of carbonic acid on carbon a proportion of 4 per cent of carbonic acid. —*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 15.

THE PROGRESS MADE IN THE CELLULOSE INDUSTRY.

By Dr. C. O. WEBER.

Within the last three or four years the domain of the industrial application of cellulose has been enriched by a new product, which constitutes the point of departure of a whole series of homologous bodies, some of which are certainly destined to play an important part from the industrial point of view. This is acetate of cellulose, prepared by a method discovered by Cross and Bevan. The originality of the process is represented by the following equation:—

$$C_6H_{10}O_5+Mg(C_2H_3O_2)_2+2CH_3COCl=$$
$$=C_6H_6O_5(C_2H_3O_2)_4+MgCl_2+2H_2O.$$

The industrial importance of this process rests in the fact that only two acetyls are obtained from chloride of acetyl and at a high price, while the two others are prepared with acetate of magnesium, and with ordinary acid. It is supposed *a priori* that this same body, acetate of cellulose, can be obtained by the action of acetic anhydride on cellulose, for it is extremely probable that in the above reaction, there is first of all an action of the chloride of acetyl on the acetate of magnesium, with the formation of acetic anhydride. In reality we cannot effect the transformation of cellulose into the tetracetate by means of acetic anhydride; we can only obtain a tri-acetate with properties of no particular value. Even to effect this result such an enormous excess of anhydride must be used that the commercial production of this acetate would have no chance of success owing to the great expense involved.

The manufacture of tetracetate of cellulose by Cross and Bevan's process is already being carried on on a large scale, as is also the manufacture of tetrabutyrate of cellulose, prepared in an analogous manner.

Besides these ethers of cellulose, we at present know nothing beyond the nitrates of cellulose, which are distinguished from the former by their explosive properties. The ethers are not inflammable, and only burn imperfectly. With solvents they behave in the same manner as the nitrates, in so far that all their solutions are of a colloidal nature, but they differ from the nitrates with regard to the extent of their solubility. The acetate is completely insoluble in methylic and ethylic alcohols, acetate of ethyl, acetate of amyl, acetone, and ether; but, on the other hand, it is soluble in benzoate of ethyl, chloroform, epichlorhydrine, acetic anhydride, glacial acetic acid, and nitrobenzene. The solution of the acetate in this last

substance becomes on cooling a solid but completely transparent jelly. A fact to be noted is that the solutions of the tetracetate in chloroform, epichlorhydrine, or benzoate of ethyl can be diluted with acetone without the slightest precipitation taking place. When evaporated on a plate of glass, the solutions of the acetate leave residues in the form of particles or filaments of great transparency.

The acetate resists the action of reagents in a remarkable manner; dilute acids, with the exception of nitric acid, do not attack it at all, and the same is the case with alkaline lyes, even at a high temperature, while these reagents completely destroy the nitrates even in the cold.

When boiled for several hours with an alcoholic solution of soda, very fine particles are completely saponified, but the saponification does not disintegrate the material so that the particles retain their form and transparency.

The insulating properties of the acetate are also worthy of notice, properties which considerably surpass those of indiarubber and guttapercha.

The acetate is very durable and does not begin to soften below a temperature of 150°, and this change is not accompanied by any destruction of material.

The hydrate of cellulose is entirely analogous with the acetate, from the point of view of its chemical properties, its resistance to the action of reagents and to high temperatures; but it is more soluble than the acetate in the solvents mentioned above, and it is easily soluble in acetate of ethyl and in acetone.

The filaments prepared from the butyrate closely resemble those formed from the acetate, but they are a little more flexible and softer.

These properties clearly show the commercial importance of the acetate and the butyrate of cellulose, and it is certain that these substances will soon become powerful rivals of celluloid in certain of its applications. This will be especially the case when there is an advantage in using a non-inflammable material, in preference to one eminently inflammable. Further, on account of their non-inflammability, their resistance to the action of moisture and high temperature, and their high insulating properties, these cellulose ethers can easily replace mica and be employed as an insulator, &c. It is also certain that these bodies can be advantageously used as metallic lacquers, for their resistance to atmospheric influences render them unique in this respect; in fact, we can safely predict a prosperous future for the butyrate and acetate of cellulose.—*Zeitschrift fur Angewandte Chemie*, 1899, p. 5.

THE CHEMICAL ANALYSIS OF ROCKS: ESTIMATION OF POTASSIUM AND SODIUM.

By ED. BONJEAN.

In a recent communication made to the Academy of Sciences (*Comptes Rendus*, cxxviii., May 1, 1899) by Michel Lévy, "On the Separation into Two Natural Groups of the Volcanic Overflow of Mont Dore; Distinctive Chemical Characteristics of their Magmas and of the Material which has Fed the Eruptions of the Puys Range," results of the analysis of eleven volcanic rocks obtained from the periphery of the crater of Mont Dore were given; the analyses were afterwards reproduced here. It was very important to determine exactly the respective quantities of soda and potash in these rocks. The following was the method used by preference, instead of any previously known one, after having proved the exactness of our method many times by the chemical analysis of waters and rocks. This process requires a good deal of time and care. Unfortunately the quantities of soda and potash cannot be exactly determined until after having completely isolated the salts of these two alkaline metals in a state of absolute purity.

Method of Analysis.

1. The silica was determined as well as the oxide of iron and aluminium; the lime, magnesia, and sulphuric acid after attacking the rock with alkaline carbonates.

2. The attack with carbonate of lime (1 grm. of rock to 0·5 grm. of carbonate of lime) was effected in a Forquignon-Leclerc furnace, for the estimation of the alkaline metals. The amount of silica is checked. As for the oxides of iron and aluminium, the lime, and magnesia, the results here obtained are generally incorrect, no matter what care may be used in the separation of these bodies, on account of the dissemination of the large quantity of lime added. The separation and estimation of the potash and soda are effected in the following manner:—The silica, oxide of iron, aluminium, and lime are eliminated in the ordinary manner. The remaining solution is evaporated to dryness on the water-bath, and the ammoniacal salts (oxalate, acetate, and chlorhydrate) are driven off by heat. Take up with water, and separate the magnesia in the form of ammonio-magnesic phosphate; this is the only manner in which it can be entirely got rid of. The ammonia is driven off, and the phosphate of ammonia precipitated by a fresh solution of pure neutral acetate of lead at 10 per cent in large excess. Filter and remove the excess of lead by means of sulphuretted hydrogen. After filtration and evaporation of the liquid on the water-bath, the residue is heated to dull redness, taken up with very dilute hydrochloric acid, filtered, and concentrated. The potassium is precipitated by chloride of platinum with alcoholic ether added. Filter, and wash with alcoholic ether; dissolve the chloroplatinate of potassium in warm water; displace the platinum by magnesium; filter, wash, incinerate, and weigh; the platinum precipitated corresponds to the potassium.

From the solution separated from the $PtCl_4 2KCl$, the alcoholic ether is driven off by heating, the platinum is precipitated with SH_2 while hot; this is then filtered, evaporated, and the residue brought to a red heat after the addition of sulphuric acid. This leaves sulphate of soda, which is weighed and can then be crystallised.

Chemical Analysis of Eleven Volcanic Rocks.

I. Phenolite from Roc Blanc.
II. Phenolite from Malvialle.

	I.	II.
SiO_2	58·70	54·97
Al_2O_3	22·36	25·84
Fe_2O_3	5·08	6·29
MgO	1·27	1·13
CaO	3·39	5·21
K_2O	5·45	3·52
Na_2O	5·13	4·49
SO_3	Traces	—
P_2O_5	—	Traces
	101·38	101·45

III. Trachyte in large crystals from Quenille.

	III.
SiO_2	56·36
Al_2O_3	21·32
Fe_2O_3	7·29
MgO	2·06
CaO	5·07
K_2O	3·65
Na_2O	6·17
SO_3	—
P_2O_5	—
	101·92

IV. Tephritic haüyne, below l'Aiguiller de Guéry (slightly decomposed).
V. Tephritic haüyne, between Quenille and Puy-Loup.

VI. Tephritic haüyne, under the Roc Blanc.
VII. Tephritic haüyne, under the Roc Blanc (slightly decomposed).
VIII. Tephritic haüyne, under the Roc Blanc.

	IV.	V.	VI.	VII.	VIII.
SiO_2	54·00	53·60	53·20	53·00	52·80
Al_2O_3 . ..	24·10	22·57	24·16	22·63	21·95
Fe_2O_3 ..	8·95	6·78	7·07	7·50	10·96
MgO	2·35	3·92	2·20	2·47	3·06
CaO	4·65	5·80	6·38	7·14	7·05
K_2O	1·58	4·01	3·21	5·89	2·39
Na_2O . ..	5·60	5·11	4·44	1·72	4·37
SO_3	—	Traces	0·50	0·25	—
P_2O_5	—	—	—	—	—
	101·23	101·79	100·16	100·60	102·58

IX. Ophitic basalt, below Ordenche.
X. Basalt from Puy-Loup.
XI. Compact basalt from the summit of Ordenche.

	IX.	X.	XI.
SiO_2	49·00	47·23	44·50
Al_2O_3	21·70	24·25	21·50
Fe_2O_3	13·30	11·33	14·90
MgO	5·22	4·85	7·60
CaO	8·95	8·47	8·96
K_2O	1·95	1·64	2·47
Na_2O	0·63	1·81	1·36
SO_3	—	—	—
P_2O_5	—	—	—
	100·75	99·58	101·26

—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 14.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To the Water Examiner, Metropolis Water Act, 1871.

London, November 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during October was 2·59 inches, of which 2·22 inches fell on four days, viz., the 1st, 26th, 27th, and 29th; the heaviest fall was on the 27th, when 0·9 inch fell. The average rainfall for this month is 2·75 inches; we thus find a deficiency of 0·16 inch, bringing the total deficit for the year up to 3·84 inches, or 18·1 per cent on the thirty years' average.

Our bacteriological examinations of 386 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, stand-pipes, &c., making a total of 425 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	290
New River, filtered (mean of 78 samples) ..	10
Thames, unfiltered (mean of 26 samples) ..	1367
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 204 samples)	20
Ditto ditto .. .. highest	341
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	876
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	21

The chemical and bacteriological analyses for the month show that the supply of water to the metropolis continues to be highly satisfactory.

Our attention has been drawn to the Report of the Proceedings of the London County Council for the 24th of October, where it is stated, on pp. 1433-34, that there exists a variation between the results of analyses made by the late Sir E. Frankland and ourselves. It is remarked that while Sir E. Frankland found the highest proportion of organic carbon during the month of July last in the water supplied by the Lambeth Company, our results showed the water of the Grand Junction Company to contain the highest average amount of organic carbon. We give here the actual figures:—

	Organic Carbon in parts per 100,000. Sir E. Frankland. (One analysis).	Ourselves. (Mean of 4 analyses).
Lambeth	0·123	0·123
Grand Junction (Kew) ..	0·118	0·134
Grand Junction (Hampton)	—	0·126

Again, in the same Report, it is said that in August Dr. Percy Frankland found the highest proportion of organic carbon in the Lambeth and Chelsea waters, while we found the highest average amount in the water from the Southwark and Vauxhall Company. Here also we give the actual figures:—

	Organic Carbon in parts per 100,000. Dr. P. Frankland. (One analysis).	Ourselves. (Mean of 4 analyses).
Lambeth	0·118	0·128
Chelsea	0·118	0·120
Southwark and Vauxhall..	0·110	0·130

We must point out that the above figures are remarkably concordant, the variations being confined to the second and third places of decimals; the actual variations between our respective results being less than one part per million. So close an agreement between different chemists on samples taken on different days is very striking, and instead of the figures being characteristic of any discrepancy, they are practically identical, considering the nature of the analysis.

The statement on p. 1434 of the above-quoted Report, that our samples for chemical analysis are taken from the Water Companies' clear water wells, is inaccurate. Our Reports state that the samples are taken from the Companies' mains in various parts of London, some of them being drawn from the identical stand-pipes whence Sir E. Frankland's samples were taken.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE VARIATION IN THE COMPOSITION OF "PARIS GREEN," WITH SCHEME FOR ANALYSIS.*

By THOMAS B. STILLMAN, Ph.D.

The increasing consumption of Paris green (also called Schweinfurt green, French green, Mitis green, Emerald green), especially in horticultural work, has developed a manufacturing industry that a few years ago was of small magnitude; its principal use, before 1870, being as a green pigment, with price varying from 30 cents to 40 cents per pound. For this purpose, however, it never ranked as a permanent colour ("Paints, Colours, Oils, and Varnishes," G. H. Hurst, p. 170), and its manufacture was gradually decreasing when its use as an insecticide developed.

In 1896 the manufacture increased to such an extent that the price was reduced to 17 cents per pound, and at the present time is quoted at 12½ cents per pound.

The article as formerly prepared for pigment purposes was of uniform composition, or nearly so; but of late years, either in hurrying the manufacture or by needlessly adding excess of arsenious oxide, the variation in composition is very marked.

Not only is this so of the production by any one manufacturer of his various outputs, but if samples be taken at random in the market it is seldom that two can be found of similar composition. This has led to many complaints by the dealer and by the horticulturist; by the former, that he, with the aid of the chemist, has found the composition not constant; and by the latter, that Paris green fails in many instances as an insecticide, since it is well known that, with certain percentages of arsenious oxide, combined as arsenite therein, the action is nil.

When pure, the composition of Paris green may be stated as an aceto-arsenite of copper—a combination of arsenious acid, oxide of copper, and acetic acid; having CuO 31·29 per cent, As_2O_3 58·65 per cent, and acetic acid 10·06 per cent ("Report N.J. Agricultural Experiment Station," 1897, p. 408).

This formula is empirical, since a portion of the arsenic may exist as arsenic acid as well as arsenious acid, and copper suboxide may be present in small amounts with the copper oxide.

Adulteration, in the sense of foreign material added, is rare with the manufacturers of Paris green in this country, and I have failed to find recorded any analyses showing contamination with barium sulphate or calcium carbonate.

The following analyses, in 1897, made by Mr. W. S. Myers, Chemist at the State Agricultural College, New Brunswick, N.J. ("Report N.J. Agricultural Experiment Station," 1897, p. 408) will show the variation in the amounts of As_2O_3 in the samples of Paris green submitted to him:—

Manufacturer.	Dealer.	As_2O_3.
John Lucas and Co.	J. J. Collins and Son	47·82 p.c.
Wetherell and Co.	From manufacturer	64·88 ,,
Unknown	J. B. Anistaki	56·19 ,,
Cawley, Clark, and Co.	C. Ribsam and Sons	68·59 ,,
C. T. Raynolds	Wm. Rust and Sons	58·44 ,,
Cawley, Clark, and Co.	Freehold Grange	41·54 ,,
Robert Shoemaker	From manufacturer	56·03 ,,
John Lucas and Co.	J. J. Collins and Son	63·11 ,,
Leggett and Bro.	Wm. Rust and Sons	59·33 ,,

Mr. Myers found no adulteration whatever in any of the samples, but the percentage of As_2O_3 in many was excessive, and as this chemical is cheaper than the other constituents, fraud would be indicated in this direction.

Messrs. Cawley, Clark, and Co., manufacturers, in reply to question of guaranteeing the percentage of arsenite, state:—"We do not make many assays of our green, but we have made several at considerable intervals, and found the composition approximately constant. We have another check which confirms this, viz., by weighing each batch, and we find from given amounts of materials that yield is sensibly constant. As our green is composed only of arsenious acid, copper oxide, and combined acetic acid, a simple calculation will show you that the cost of production would be lessened by increasing the percentage of arsenic."

Messrs. John Lucas and Co. state:—"The only explanation we could give you for the variation in the amounts of arsenic is found in the well-known fact that most tests or formulæ for products rarely have a definite or absolute proportion assigned—or, in other words, considerable latitude is allowed, unless the product may be one that is little called for. The theoretical combination, as stated by Mr. Smith, is 58·65 per cent, but Paris green is made in large batches of 5, 10, or 20 tons, and at certain seasons of the year the manufacturer is urged to the utmost to turn it out fast enough; hence sufficient time is not given to the process or the variation would not be more than 5 per cent either way as compared with the theory."

John B. Smith, Sc.D., State Entomologist, N.J., comments as follows ("Report Agricultural Experiment Station, N.J.," 1897, p. 411):—

"Though not directly so stated, these gentlemen admit the possibility of a variation as great as 15 per cent in their product, but seem to consider it immaterial from a practical standpoint. In this I must dissent, for a difference of even 10 per cent of arsenic may make all the difference between an effective and ineffective application. From all the facts obtainable it seems certain that Paris green varies in the percentage of arsenic under the best conditions, and that it may be present either as an arsenite or as an arsenate. Manufactured in large quantities, the difficulties in obtaining a satisfactory result increase, so that a *difference of 25 per cent may exist in an absolutely unadulterated product.* It follows that, as has been practically found by farmers, the material is not reliable and results are not constant."

In reply to a letter from the writer to Prof. Voorhees, Director of the N.J. Agricultural Experimental Stations, regarding adulteration of Paris green, the following communication was received:—

New Jersey Agricultural Experimental Stations,
New Brunswick, N.J., May 11th, 1898.
EDWARD B. VOORHEES, Director.

Dr. THOMAS B. STILLMAN, Hoboken, N.J.

DEAR SIR,—I have your letter of the 10th inst. concerning the adulteration of "Paris green." I have to say in reply, that in our experience, there is a very wide variation in the composition of different samples of "Paris green," but thus far we have been unable to positively detect adulterations. "Paris green" has also been examined for adulteration in Massachusetts and in Alabama, but in neither State have they been able to find any serious adulteration.

Very truly yours,
E. B. VOORHEES.

Paris green* manufactured in Germany is often adulterated with barium sulphate. Post ("Technisch-chemische Analyse," p. 367) mentions the following as added impurities:—Barium sulphate, calcium carbonate, chrome yellow, and iron oxide.

Wagner ("Chemical Technology," p. 458) states:—"Schweinfurt green (Paris green), in Germany, is known under a number of aliases derived from the peculiar depth of hue as modified in various manufactories by means of barium sulphate, lead sulphate, and chrome yellow.

N. Reitter ("Wittsteins Vierteljahrschrift," VII., p. 359) analysed two samples of Paris green ("Schweinfurt grün") of German manufacture, with the following results:—

* Scheele's green is often mistaken for Paris green, since it is also an arsenite of copper; it, however, contains no acetate, its formula being $CuAs_2O_3.CuO.2H_2O$.

From *The Stevens Indicator*, vol. xv., No. 3.

	No. 1. Per cent.	No. 2. Per cent.
Copper oxide (CuO)	29·370	29·181
Arsenious acid (As_2O_3) ..	48·070	46·839
Acetic acid	6·628	10·230
Water	2·500	2·500
Barium sulphate..	13·432	11·250
	100·000	100·000

C. Reinhard ("Wagner's Theorie und Praxis de Gewerbe," Bd. i., p. 489) found in two varieties of Paris green, chromate of lead, and in one sulphate of barium. Thus:—

	No. 1. Per cent.	No. 2. Per cent.
Copper oxide (CuO)	21·77	24·31
Arsenious acid (As_2O_3) ..	40·28	52·42
Acetic acid	6·20	8·86
Chromate of lead	6·56	14·41
Barium sulphate	25·19	—
	100·00	100·00

Dammer ("Handbuch der Chemischen Technologie," 1898, v., p. 556) states that Schweinfurter-grün has several trade names in Germany, depending upon its composition, as follows:—Englischgrün, Patentgrün, Hörmann's grün, Papageigrün, Kaisergrün, Königsgrün, Wienergrün, Kirchbergergrün, Leipzigergrün, Zwickauergrün, Baselergrün, Parisergrün, Neuwiedergrün, Würzburgergrün, and Jasnügergrün. Variation in colour is produced by the addition of any of the following substances:—Gypsum, barium sulphate, chromate of lead, zinc yellow, sulphate of lead, calcium carbonate, &c.

The employment of chromate of lead has a special use in the lightening of the colour for use of the pigment in the textile industries, such as in wall-paper, tapestry, &c., but not in its use as an insecticide.

As chromate of lead is much more expensive than arsenious acid, the conclusion reached in regard to adulteration would be that Paris green, manufactured in this country and used in horticultural work, is practically free from adulteration, whereas, if manufactured for use as a colour with various shades of green, it may contain all the substances enumerated above in addition to the constituents requisite for its manufacture.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 2nd, 1899.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MESSRS. F. J. Beale, George Young, H. Royal-Dawson, E. T. Shelbourn, S. J. Peachey, H. A. Thiersch, R. W. Lindsay, S. Dickson, F. N. A. Fleischmann, and C. Simmonds, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James William Anderson, 1, Preston Villas, Halling, Kent: Francis Paul Armitage, High House, Brook Green, Hammersmith, W.; Frederick William Armstrong, The Hill, Langport, Somerset; Frederic Arnold Beesley, Bank House, Wirksworth, Derby; Edgar Marsh Chapman, 17, Bloomsbury Square, W.C.; John Arthur Dewhirst, 125, Mount View Road, Stroud Green, N.: Frank Rawlinson Duddridge, 45, Sidney Grove, Newcastle-on-Tyne; Herbert Frederick Francis Burdett Fermor, 15, Ansdell Road, Peckham, S.E.; Elliott Henry Gurney, Albert Street, Marrickville, New South Wales; Henry Wulff Kinnersley, 4, The Avenue, Keynsham, Somerset; William Thomas Leeming, 60, Lomeshaye Road, Nelson; Stephen Joshua Lett, 25, Percy Street, Liverpool; Edward Watkin Lewis, 64, Ommaney Road, New Cross, S.E.; Wm. D. McCreath, The Plains, Totnes, S. Devon; Harry Ainley Neale, Brentwood, Clothorn Road, Didsbury, Manchester; Thomas Henry Palmer, "Amalfi," Longueville, Sydney, New South Wales; Marchant Pearson, The Grammar School, Bridlington; Bennett C. Polkinghorne, 46, Lynette Avenue, Clapham Common, S.W.; Georges Ponthieu, Pharmacie Centrale de France, Avenue de Paris, St. Denis, Seine; William Downing Raynor, 13, Christ Church Road, Doncaster; Christopher Foulis Roundell, Guards' Club, Pall Mall, S.W.; William Russell, Thetford, Norfolk; Robert Hawks Walton, 424, Park Road, Moore Park, Sydney, N.S.W.; F. R. Leyland Wilson, Charterhouse, Godalming; John Wilson, 73, Melford Road, Leytonstone, E.

The Chairman referred to the great loss the Society had sustained through the deaths of its illustrious former President, Sir Edward Frankland, and its Foreign Member, Professor Bunsen.

Of the following papers those marked * were read:—

*120. "*On Methods for Determining the Relative Proportions of Gaseous Chloroform and Air in a Mixture of the Two, and on a Method for producing a Mixture of Air and Chloroform in any Desired Proportion.*" By A. VERNON HARCOURT.

To produce anæsthesia, air is inhaled mixed with a small percentage of chloroform vapour. The proportion of chloroform most suitable for this purpose has not been determined, probably for want of a good chemical method of making this determination. The reaction which takes place between chloroform and a hot alcoholic solution of potash, $CHCl_3+4KOH=3KCl+HCO_2K+2H_2O$, seemed to furnish a basis for such a method. However, with regard to this reaction, two statements have been made, that all the chlorine of chloroform can thus be converted into a chloride and that it cannot. The author has worked out and described a method for removing chloroform vapour from air, and obtaining chloride from it by means of the above reaction; but on applying the method to weighed quantities of chloroform the results were always about 4 per cent too low. This error is so nearly constant that the method may be used and the results increased by 4 per cent.

A better method depending on a reaction (which, as far as the author knows, is new) has since been worked out by him.

When the mixture of air and chloroform is mixed with a certain proportion of steam by heating it with a few c.c. of water to 50° or 60°, and a platinum wire is kept in a state of incandescence in this mixture, the whole of the chloroform undergoes the following change.—

$$2CHCl_3+2H_2O+O_2=6HCl+2CO_2.$$

With a fairly bright wire the change is complete in an hour, and the hydrogen chloride may be obtained in dilute solution by bringing in 20 c.c. of water, and may be determined in the flask with a standard solution of ammonia. If enough steam is not present, or the platinum wire is not heated beyond a low incandescence, or sufficient time is not allowed, a smell of chlorine will be observed at the mouth of the flask and the result will be too low. It was ascertained incidentally that a weighed quantity of chlorine, treated as above, is completely converted into hydrogen chloride. Doubtless the changes—

$$2H_2O+2Cl_2 \leftrightharpoons 4HCl+O_2$$

both occur, but the water present gradually withdraws all hydrogen chloride from the system.

The author also described a method of producing a mixture of air and chloroform in any desired proportion and of constant composition. This consisted in blowing air through a mixture of chloroform and alcohol. The density of the liquid, showing the proportion of its ingredients, could be observed during the passage of the air by

means of two little glass bulbs, of which one floated and one sank when the density was right, and be adjusted by additions of chloroform. Density and temperature being constant, the proportion of chloroform taken up by the air was constant also. To remove alcohol vapour, the current of air was then passed through two wash-bottles containing sulphuric acid and water respectively.

DISCUSSION.

In reply to remarks by Mr. Hehner and Dr. Perkin, Mr. HARCOURT said he doubted whether the use of a Lux balance for observing the density of the gas-stream would be as convenient as the Wolfe's bottle with two floats which he had used. The great difference in density of alcohol and chloroform made the density of the liquid in this case a good index of its composition. He thought a liquid less volatile than alcohol might be found and might have advantages; but alcohol answered well, was innocuous even if a little of its vapour passed on, and could easily be got pure.

*121. "*The Theory of Saponification.*" By J. LEWKOWITSCH.

The author showed that the view of the theory of saponification, according to which the hydrolysis of triglycerides is considered a tetramolecular reaction, must be abandoned in favour of the theory propounded by Geitel, who regards the reaction as bimolecular. If this be so, diglycerides and monoglycerides should occur in partially hydrolysed fats. The author has demonstrated their presence by acetylating the intermediate products, freed from glycerol, and proving that the acetylated products exhibit considerable acetyl values, which rise and fall with the progress of saponification. Additional proof was obtained by determining the amounts of the insoluble fatty acids of the acetylated products, and also their saponification values. The curves illustrating these two series of values correspond to the acetyl curves in a very satisfactory manner.

DISCUSSION.

Dr. LEWKOWITSCH said, in reply to questions from Mr. Blount and Mr. Hehner, that he had not tried any other methods beyond those mentioned, as, in his opinion, they were sufficient to give a satisfactory answer to the point at issue. The proportion of glycerine in the partially saponified samples might have been determined as a further proof, but the methods employed were shorter and more reliable. The saponification had been carried out in a manner corresponding to operations on a large scale, and, since the steam pressure alone causes a very violent boiling and mixing of the mass, there could be little doubt that the samples taken did represent the average. He had not made use of water as a saponifying agent.

*122. "*Note on the Action of Dilute Nitric Acid upon Oleic and Elaidic Acids.*" By F. G. EDMED, B.Sc.

In the course of some experiments on the oxidising action of nitric acid upon oleic acid, the author found that, by using nitric acid of sp. g. 1·2—1·3, the sole action was an isomeric change from oleic to elaidic acid. If the density of the acid did not exceed 1·25 and the action took place in the cold, the yield of the elaidic acid was quantitative. Increase in the strength of the nitric acid and rise of temperature diminished the yield. The rapidity of the change was dependent on the purity of the oleic acid. The dilute nitric acid used in the experiments was carefully freed, by prolonged boiling, from nitrous acid, which is known to bring about a similar change.

Nitric acid of the strengths indicated above has no action in the cold upon elaidic acid itself. Hot concentrated nitric acid decomposes it only upon prolonged boiling.

DISCUSSION.

Mr. EDMED said, in reply to Dr. LEWKOWITSCH, that the specimen of elaidic acid thus prepared melted at 45° C.

*123. "*Formation of Tetrazoline.*" By S. RUHEMANN and H. E. STAPLETON.

On heating monoformylhydrazide at 210—220° for about six hours, the authors obtained a good yield of tetrazoline,—

$$CH\leqslant^{NH\cdot N}_{N\cdot NH}\geqslant CH.$$

The hydrochloride of this base, $C_2H_4N_4,HCl$, had been prepared recently by Pellizzari (*Atti R. Accad. dei Lincei*, 1899, [v], viii., I, 327) by heating diformylhydrazide and treating the crystalline product thus formed with hydrochloric acid. The authors find the melting-point of this salt to be 151—152°. The free base is extremely soluble in alcohol and in chloroform, sparingly so in petroleum-ether. It crystallises from a mixture of chloroform and alcohol in colourless needles which melt at 82—83°, are very deliquescent, and give with copper sulphate a blue colouration. The picrate, $C_2H_4N_4,C_6H_2(NO_2)_3OH$, forms yellow prisms, soluble in alcohol only with great difficulty.

DISCUSSION.

Dr. GEORGE YOUNG said that the authors of this paper had discarded the name dihydrotetrazine in favour of tetrazoline, the term introduced by Pellizzari. This was to be regretted as tending to confusion in the nomenclature of the carbo-nitrogen cyclic compounds. Dihydropyrrole was known as pyrroline, dihydropyrazole as pyrazoline. Tetrazoline should denote dihydrotetrazole, and not dihydrotetrazine. The name isotetrazoline was in use for certain dihydro-derivatives of tetrazole.

Mr. STAPLETON, in reply, said that although the alteration by Pellizzari of the name dihydrotetrazine into tetrazoline was perhaps not altogether satisfactory, it had been accepted both by Pinner and Bamberger, and accordingly the authors of the paper had not hesitated to employ the term.

*124. "*Asymmetric Optically Active Nitrogen Compounds. Dextro- and Lævo-benzylphenylallylmethylammonium Iodides and Bromides.*" By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

On heating the α benzylphenylallylmethylammonium iodide prepared by Wedekind (*Ber.*, 1899, xxxii., 517) with one molecular proportion of silver dextrocamphorsulphonate dissolved in acetone and ethyl acetate, filtering, and evaporating to dryness, a crystalline residue was obtained which by fractional crystallisation from solution in acetone and ethyl acetate, may be resolved into the less soluble constituent, *dextro-α-benzylphenylallylmethylammonium dextrocamphorsulphonate*,—

$$N(C_7H_7)Ph(C_3H_5)MeC_{10}H_{15}OSO_3,$$

and the more soluble isomeric dextrocamphorsulphonate of the *lævo-base*; the former has the molecular rotation in aqueous solution $[M]_D=+208°$, and the latter $[M]_D=-87°$.

On adding potassium iodide or bromide to aqueous solutions of these salts, the corresponding iodide or bromide is precipitated, and may be purified by crystallisation from alcohol; the following salts were thus obtained: —*Dextro-α-benzylphenylallylmethylammonium iodide*, $N(C_7H_7)Ph(C_3H_5)MeI$ $[\alpha]_D=+52·4°$. *Dextro-α-benzylphenylallylmethylammonium bromide*,—

$$N(C_7H_7)Ph(C_3H_5)MeBr\ [\alpha]_D=+68·6°.$$

Lævo-α-benzylphenylallylmethylammonium iodide, $[\alpha]_D=-51·4°$. *Lævo-α-benzylphenylallylmethylammonium bromide*, $[\alpha]_D=-67·3°$.

The isolation of these compounds proves that dissolved substances may owe their optical activity to the asymmetry of nitrogen.

It is further shown that Wedekind's iodide is not a racemic compound, but merely an ordinary or pseudo-racemic mixture of the dextro- and lævo-components.

DISCUSSION.

Dr. ARMSTRONG thought this communication was the

most valuable contribution made to stereochemistry since the introduction of geometrical considerations by Le Bel and van 't Hoff.

The discovery of a method of preparing asymmetric nitrogen compounds was not only of intrinsic importance, but afforded a means of investigating the problem which chemists had so long disputed as to the valency of nitrogen in ammonium compounds. It would perhaps be possible, by varying the number of radicles, to discriminate between compounds containing pentad and "molecular" compounds containing triad nitrogen.

Dr. LEWKOWITSCH said he fully appreciated the difficulties attendant on work of this kind, as some time ago he had attempted to prepare silicon compounds possessing optical activity, but so far without success. He ventured to suggest that these experiments might now be resumed.

125. "*Camphoroxime.* Part III. *Behaviour of Camphoroxime towards Potassium Hypobromite.*" By M. O. FORSTER, Ph.D., D.Sc.

With the object of preparing brominated derivatives of camphoroxime, the author has studied the behaviour of this substance towards alkaline hypobromite.

The *compound*, $C_{10}H_{16}BrNO_2$, obtained by the action of a concentrated ice-cold solution of potassium hypobromite on camphoroxime, crystallises from alcohol in snow-white, fern-like aggregates, and melts at 220° to a colourless liquid which immediately decomposes; it gives Liebermann's reaction for nitroso-derivatives, and yields camphoroxime on reduction with zinc dust and acetic acid. A 2 per cent solution in benzene gave $[\alpha]_D = -65{\cdot}6°$.

The *compound*, $C_{10}H_{14}BrNO$, produced when the foregoing substance is dissolved in concentrated sulphuric acid, crystallises from alcohol in lustrous transparent prisms; it shrinks and darkens at about 210°, becoming completely charred at 220°. This derivative is optically inactive, and does not give Liebermann's reaction. Treatment with hot concentrated hydrochloric acid converts it into an *isomeride*, which separates from alcohol in large transparent six-sided crystals, and melts to a colourless liquid at 240°; this modification is likewise optically inactive, and does not give Liebermann's reaction; it yields a *benzoyl* derivative, which crystallises from alcohol in lustrous scales melting at 174—176°.

The *nitrile*, $C_9H_{13}N$, obtained when either of the compounds, $C_{10}H_{14}BrNO$, is heated with aqueous soda, forms a limpid, fragrant oil which boils at 198—199° under 760 m.m. pressure, and has sp. gr. 0·9038 at 24°; it is oxidised by an ice-cold solution of potassium permanganate, and instantly decolourises a solution of bromine in chloroform.

The *amide*, $C_9H_{15}NO$, occurs as a by-product in the preparation of the nitrile, and is formed when that substance is heated with alcoholic potash; it crystallises from light petroleum in white, highly lustrous needles melting at 90°. When this compound is heated with hydrochloric acid, isolauronolamide and isolauronolic acid are produced, and as campholytic acid is converted by mineral acids into isolauronolic acid, it appears probable that the new amide is the hitherto unknown amide of campholytic acid. Experiments are being conducted with the view of ascertaining if this is so.

126. "*Optical Influence of an Unsaturated Linkage on certain Derivatives of Bornylamine.*" By M. O. FORSTER.

Condensation products of bornylamine with aromatic aldehydes have been prepared in order to compare the optical activity of such compounds with the corresponding derivatives of benzylbornylamine.

It is found that transition from benzylbornylamine and its nitro-derivatives to the corresponding benzylidene compounds is attended by a fall in the rotatory power of the benzene and alcoholic solutions; the decrease in the case of the paranitro-derivatives approximates to the rotational difference between benzylbornylamine and benzylidene bornylamine, but is widely divergent from this in the case of the orthonitro-compounds.

Benzylidenebornylamine, o-*nitrobenzylidenebornylamine*, p-*nitrobenzylidenebornylamine*, o-*hydroxybenzylidenebornylamine*, and p-*hydroxybenzylidenebornylamine* are described in the paper.

127. "*The Interaction of Sodium Hydroxide and Benzaldehyde.*" By CHARLES A. KOHN, B.Sc., Ph.D., and W. TRANTOM, B.Sc., Ph.D.

The object of the investigation was to ascertain if an intermediate compound was formed in the preparation of benzyl alcohol from benzaldehyde and soda. The authors state that, in presence of water, the sole products of the reaction are benzyl alcohol and sodium benzoate. By employing carefully dried materials, however, benzyl benzoate is formed to the extent of 10 per cent. The reactions which occur are explained by the following equations:—

1. $2C_6H_5.CHO + NaOH = C_6H_5{\cdot}C(ONa)(OH)(OC_7H_7)$.
2. $C_6H_5{\cdot}C(ONa)(OH)(OC_7H_7) = C_6H_5CO_2Na + C_7H_7OH$.
3. $C_6H_5{\cdot}C(ONa)(OH)(OC_7H_7) = C_6H_5CO_2C_7H_7 + NaOH$.

Reaction 2 is favoured by the presence of water and excess of soda; reaction 3 by an excess of aldehyde.

128. "*Electrolytic Preparation of Induline Dyes.*" By E. C. SZARVASY, Ph.D.

When a mixture of aniline hydrochloride and aniline is fused and electrolysed under given conditions, induline colouring matters are formed. The author describes the apparatus he constructed to carry out these experiments. The following products were separated:—

Induline, $C_{18}H_{13}N_3$; B4, anilidoinduline, $C_{24}H_{18}N_4$; induline 6B, $C_{30}H_{23}N_5$; and azophenine, $C_{36}H_{29}N_5$.

The results prove (1) that the chlorine produced by the electrolytic decomposition of the aniline hydrochloride effects diazotisation, (2) that under certain conditions the azo-compounds thus formed react with the hydrochloride of aniline, forming (3) primarily azophenine, (4) ultimately indulines.

129. "*The Heat of Combination of Copper with Zinc.*" By T. J. BAKER, B.Sc.

The only work in this direction hitherto appears to be by Dr. Galt (*Rep. Brit. Ass.*, 1898, and *Proc. Roy. Soc. Edin.*, 1899) and by Herschkowitsch (*Zeit. f. Phys. Chem.*, 1898, xxvii., 123). Neither appeared until this work was nearly completed, and in each case the number of observations appears to have been small. In the present research the method consisted in the determination of the difference between the heat of solution of an alloy of the two metals and that of an equal weight of a mixture in the same proportions. Actual determinations of the latter quantity were made, as it was not found possible to calculate it exactly from the heat of solution of the separate metals.

Two solvents were used. (*a*) Chlorine water—0·15 normal. (*b*) $HNO_3.3H_2O$.

Only alloys with less than 42 per cent copper could be so finely powdered as to dissolve quickly in chlorine water. With nitric acid as solvent, a series of twenty-one alloys—all made from the purest metals obtainable and carefully analysed—was examined. The results obtained by both methods agree very well.

The results are expressed in the form of a curve with percentages of copper as abscissæ and heats of formation of 1 grm. of alloy as ordinates. From 0 to 30 per cent of copper no heat of combination could be detected. This renders doubtful the existence of the supposed compound, $CuZn_2$ (Laurie, Charpy, and Hershkowitsch).

From 30 to 62 per cent of copper, the curve rises to an ill-defined maximum of 46 calories per grm. of alloy. This alloy (62 per cent copper) does not correspond to any simple atomic compound, but is otherwise remarkable (see 4th Report of the Alloys Research Committee, Institution of Mechanical Engineers).

From 62 per cent copper onwards, the curve gradually sinks to zero at 100 per cent copper.

Hence copper and zinc evolve heat when alloying with

one another, a point of interest with reference to the electro-deposition of brass.

The bearing of these experiments on Lord Kelvin's estimate of the limits of molecular dimensions is briefly discussed.

130. "*The Action of Sulphuric Acid on Fenchone.*" By J. E. Marsh.

The author shows that by the action of strong sulphuric acid on fenchone, aceto-xylene (Me : Me : Ac = 1 : 2 : 4) was produced in quantity approximating to the total amount required by theory, and considers this fact to be opposed to the constitution of fenchone recently put forward by Wallach and by Gardner and Cockburn.

131. "*On Glucosides.*" By Hugh Ryan, M.A.

By the action of acetochloroglucose on solutions of phenols in alcoholic potash, crystalline glucosides of the β series were obtained.

ββ-Naphthol-glucoside, $C_6H_{11}O_5{\cdot}OC_{10}H_7$, prepared from acetochloroglucose and β-naphthol, crystallises in long needles [m. p. 184—186°], is easily soluble in alcohol and in hot water, difficultly soluble in acetone, and scarcely soluble in benzene, ligroin, cold water, or ether, is readily hydrolysed either by dilute acids or emulsin, reduces Fehling's solution only after hydrolysis, is stable towards dilute alkali in which it is insoluble, and has a disagreeable taste.

β-p-Cresol-glucoside m.p. 175—177°, and *β-o-cresol-glucoside*, $C_6H_{11}O_5{\cdot}OC_6H_4CH_3$, m. p. 163—165°, resemble one another as well as naphthol-glucoside, crystallising from water in needles which are scarcely soluble in ether, benzene, or ligroin, but are fairly soluble in alcohol and in water, do not reduce Fehling's solution, are readily hydrolysed and possess a bitter taste.

β-Carvacrol-glucoside, m.p. 135°, crystallises from water in needles not readily soluble in ether or cold water, easily soluble in alcohol and in acetone, but scarcely soluble in benzene, chloroform, or ligroin. It does not refuse Fehling's solution, dissolves slowly in dilute alkali, and is hydrolysable by means of dilute acids or emulsin. Its formula is either $C_6H_{11}O_5{\cdot}OC_6H_3{\cdot}C_3H_7{\cdot}CH_3{,}\frac{1}{2}H_2O$, or

$$C_6H_{11}O_5{\cdot}C_6H_2\begin{cases}C_3H_7\\OH\\CH_3\end{cases},\tfrac{1}{2}H_2O.$$

d-Pentacetyl-glucose (m. p. 110°) is obtained by the action of 20 mols. of acetyl chloride on 1 mol. dry glucose in an open vessel.

Acetochloro galactose, a colourless semi-solid mass, was got by the action of acetyl chloride on galactose in a closed tube, and has been converted into a galactoside of β-naphthol.

(To be continued).

CORRESPONDENCE.

THE ACTION OF WATER ON MAGNESIUM.

To the Editor of the Chemical News.

Sir,—I can fully endorse one of the conclusions arrived at by Mr. Bryant in his communication published in the Chem. News of November 3rd (vol. lxxx., p. 183), for I have regularly demonstrated the production of hydrogen from water by magnesium at ordinary temperatures for the past four years, and was under the impression the fact was well known.

The junior students here, when studying the action of water on metals, by allowing them to stand in contact for a week, notice bubbles of a gas on magnesium ribbon when it is used. Later on, when they have discovered that hydrogen exists in water, their attention is directed back to the appearance of the bubbles, and the gas is collected and identified in the following way:—

About a yard of clean magnesium ribbon is loosely screwed up and placed in a four-ounce flask fitted with cork and narrow delivery tube. The flask is filled with cold water and the cork replaced, so that the whole tube is filled with water. On standing 24 hours sufficient gas may be collected to identify it.

One peculiarity about the gas so generated is that it burns with a peculiar greenish flame. Is it not possible that traces of a hydride may also be formed? This is at present under investigation.—I am, &c.,

William French.

Bury Grammar School,
Nov. 11, 1899.

LABORATORY LAMP.

To the Editor of the Chemical News.

Sir,—I should be grateful to any of your readers who can suggest a good lamp, to do the work of an ordinary Bunsen burner, for use in a country laboratory where gas is not obtainable.—I am, &c.,

Chemicus.

November 18, 1899.

NOTICES OF BOOKS.

Determination of Radicles in Carbon Compounds. By H. Meyer. Authorised Translation, by J. Bishop Tingle. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1899. Pp. x.—133. 12 mo. Ill.

Dr. Tingle's translation of Dr. Meyer's well-known book seems to be very carefully done, and will be welcomed by those instructors wishing to use it with classes in England and America. The work deals with quantitative work in organic chemistry, and is adapted for advanced students. Chapter I. deals with the determination of hydroxyl by acylation, by alkylation, by the preparation of carbamates, and by the formation of esters of phenylcarbamic acid. In Chapter II. the determination of carboxyl is treated in several ways:—A. Analysis of metallic salts of the acid. B. Titration. C. Etherification. D. Determination of the electrolytic conductivity of the sodium salts. E. Indirect methods, such as the carbonate, ammonia, hydrogen sulphide, and the iodine methods.

A valuable feature are the numerous references to literature. A few woodcuts are introduced to elucidate the subject. An Index of Authors, and a separately alphabeted Index of Subjects close the volume. The advantage of printing the indexes separately, in two alphabets, is not evident to the reviewer.

The book fills a place occupied by no other.

H. C. B.

The Manufacture of Carbons for Electric Lighting and other Purposes: a Practical Handbook. By Francis Jehl, Member of the American Institute of Electrical Engineers. London: *The Electrician* Printing and Publishing Company. Pp. 232.

The manufacture of carbons for electric lighting purposes is a business which has made very rapid strides within a comparatively short period of time, not only as regards quantity, but also in quality. It is rare indeed at the present day to see arc lamps giving a violet light, due to the presence of potash salts in the carbons. Ten or fifteen years ago such a thing was the rule rather than the exception.

We have in this volume a complete description of the art of making carbons, electrodes, &c., the various gas generators and furnaces used in carbonising, with a plan for a model factory.

The author points out that the literature on this subject

is very limited. We are of opinion that this is to be accounted for by the fact that most makers have trade secrets of great value to themselves, which they are unwilling to give to the world; for this we cannot blame them.

The book is well printed, and contains a great deal of interesting and important information on the subject.

The Rise and Development of the Liquefaction of Gases. By Willett L. Hardin, Ph.D. New York: The Macmillan Company. 1899. Pp. 250.

Although the literature on this subject may be somewhat scattered, as stated by the author of this work, consisting to a great extent of notices in various technical journals, we may reasonably claim that every success which has been obtained by the few accredited workers in this domain of scientific research has been promptly notified to the readers of the Chemical News.

The name of Dewar stands out pre-eminently as that of the man who has imagined and carried out some of the boldest and most remarkable experiments in this branch of physical and chemical investigation; and, having recently succeeded in solidifying hydrogen, he may echo Alexander's lament that there are no more worlds to conquer.

The development of the methods used in this particular line of research has been accompanied by much disappointment and failure, and although liquid oxygen can now be produced at a comparatively low price, it must be remembered that the first ounce made cost many hundreds of pounds.

The author divides the progress of this work into four periods: the first being mostly historical, and not of much practical importance; the second begins with the work of Faraday, during whose time the methods of producing high pressures and low temperature were greatly developed; the third deals with critical constants, and the continuity of the gaseous and liquid states of matter; while the fourth begins with an account of the experiments of Messrs. Pictet and Cailletet in the year 1877 and extends to the present time. This last period, which only embraces a little more than twenty years, is by far the most fruitful in results; the value of which may be understood when we point out that more than one-half of this volume is devoted to this period alone.

The author has, we believe, produced the first systematic work on this subject, and deserves the thanks of the scientific world for his labour.

Edinburgh University Chemical Society. — The President delivered an address on Nov. 6th, his subject being "Bunsen." Prof. Crum Brown sketched the life of Bunsen, and gave an outline of his work, in particular the investigations of cacodyl and its compounds and the elucidation of their constitution; the invention and development of numerous analytical processes and apparatus, including the introduction of scientific and exact methods of gas analysis, of spectrum analysis, and flame reactions; the discovery of cæsium and rubidium. He gave some personal recollections of Bunsen and testified to the esteem and love with which he was universally regarded by his pupils.

Filtering Device.—Sargent and Faust (*J. Am. Chem. Soc.* xxi.). For some precipitates, as MnO_2, phosphomolybdate, &c., a filter made of sand placed in a carbon filtering tube, and covered with a thin layer of asbestos, has been found very satisfactory. A small plug of glass wool is used below to retain the sand in place, and the filter should be washed three or four times with HNO_3 before using.—*School of Mines Quarterly*, xx., No. 4, p. 399.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 18, October 30, 1899.

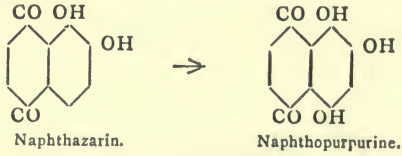
Atomic Weight of Boron.—Henri Gautier.—The author has made four series of determinations of the atomic weight of boron, which give the following numbers:—

	At. weight.	Probable error.
Using boron sulphide	11·041	±0·017
,, carbon boride	10·997	±0·017
,, boron bromide	11·021	±0·006
,, boron chloride	11·011	±0·008

The determinations carried out on boron sulphide and carbon boride, compounds very different from one another, tend to show that the atomic weight of boron is very near to 11. But in spite of the advantages resulting from their small molecular weight, these two substances are more difficult to obtain pure than the chloride and bromide. The mean of the values given above is 11·016, and is the one the author proposes to adopt. It is very near to 11 and a little greater than those previously found by Abrahall and again by Ramsay and Aston.

Mixed Anhydrides of Acyclic and Cyclic Acids.—A. Béhal.—The author has studied particularly the mixed aceto-isovaleric and acetobenzoic anhydrides. In the first case, preparing aceto-isovaleric anhydride by the methods of Gerhardt or Autenrieth, the products obtained in the two cases do not give a constant composition. The presence, therefore, of this anhydride can only be explained in three ways:—(1) The product formed is a mixture of acetic anhydride and isovaleric anhydride, and the first is more rapidly destroyed than the second by the alkaline solution. (2) The product is the mixed anhydride, and under the influence of the reagent is transformed into the alkaline acetate and isovaleric anhydride. (3) The product is a mixture of the mixed anhydride and isovaleric anhydride. The first is more easily destroyed than the second by the conditions under which it is prepared.

Naphthopurpurine, an Oxidation Product of Naphthazarine.—George F. Jaubert.—Whilst examining the action of nitric acid on Roussin's naphthazarine the author remarked that, under certain conditions, a red colouring matter is formed. An estimation of the nitrogen present showed that it was not a nitrogen derivative, but a simple product of oxidation.



Naphthazarin. Naphthopurpurine.

Sublimed naphthopurpurine is in the form of reddish brown needles, which easily melt on a strip of platinum, giving off red fumes smelling of quinone. It is not easily soluble in cold water, but very easily in hot water, from which it crystallises in tufts on cooling. It is very soluble in alcohol and acetic acid, giving a red solution. Naphthopurpurine is a trioxy-α-naphthoquinone, analysis giving—

C	58·42
H	3·05

Calculating for the formula $C_{10}H_6O_5$ the results are—

C	58·25
H	2·92

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "Enamelling upon Metals," by Henry Hardinge Cunynghame.
WEDNESDAY, 29th.—Society of Arts, 8. "The Great Seals of England," by Allan Wyon.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2088.

A BIBLIOGRAPHY OF STEEL-WORKS ANALYSIS.

By HARRY BREARLEY.

(Continued from p. 246).

MANGANESE (*continued*).

IV. VOLUMETRIC ESTIMATION OF MANGANESE.

a. Titrations with Standard Permanganate.—

87. GUYARD (*C. N.*, viii., 292).—Titration at 80° C. Associated metals are converted to peroxides, and do not interfere. The process separates Mn from alkalis, Ca, Sr. Mg, Ni, Co, Zn, and Ur. (Some of the separations are not nearly exact ones.—H. B.). Discusses three permanganates of MnO : — $5MnO.Mn_2O_7$, $4MnO.Mn_2O_7$, and $3MnO.Mn_2O_7$.

88. HABICH (*C. N.*, xii., 58).—Dilute H_2SO_4 and HCl; lower oxides of Ni and Co, ZnO, Al_2O_3, and CaO do not interfere with Guyard's process. Strong HCl or H_2SO_4, Fe_2O_3, and Cr_2O_3 render the process useless.

89. GORGEU (*J. I. S. I.*, 1894, i., 613).— Results by Guyard's process too low, partly on account of the acidity of the liquid. Donath's modification (see 100) also gives inexact results unless the solutions are slowly mixed. Criticises Guyard's views (see 87) concerning existence and constitution of the compounds formed during the titration.

90. VOLHARD (*C. N.*, xl., 207).— Manganous solution mixed with $ZnSO_4$, made faintly acid with HNO_3, and titrated near boiling-point to a permanent red colour.

91. AUCHY (*C. N.*, lxxiv., 214).—Examination of Volhard's process for estimation or Mn in steels. Add ZnO to cold solution until Fe is precipitated, then excess of ZnO; titrate at boiling-point, and deduct 0·02 per cent.

92. HASWELL (*J. I. S. I.*, 1882, 743).—Acidification with a few drops of HNO_3 previous to titration counteracts traces of organic matter. Standardise permanganate with KI and thiosulphate.

93. DAW (*C. N.*, lxxix., 25).—Titrations with permanganate are subject to error on account of organic matter, reckless addition of ZnO, and standardising solutions with Fe instead of Mn. Process described to eliminate these errors.

BREARLEY (*C. N.*, lxxix., 47) takes exception to permanganate being standardised by the Mn_3O_4 finally heated over a blast-lamp. The validity of this procedure is discussed (pages 58, 83, and 104).

94. WOLFF (*J. I. S. I.*, 1885, 301).—Separates Fe with ZnO; no filtration; excess ZnO to be avoided; $KClO_3$ used to oxidise Fe; HNO_3 leads to organic compounds, which interfere with titration. Results slightly low.

95. SARNSTROM (*C. N.*, xlvii., 177).—Sodium bicarbonate added in small quantities until Fe is precipitated; titration by Guyard's process without filtering off the Fe.

96. AUCHY (*J. C. S.*, lxxii., ii., 603).—The danger of Mn being carried down by the precipitated ferric oxide greatly lessened if about 7 grms. $(NH_4)Cl$ is added before the sodium carbonate in Sarnstrom's process.

97. MIXER and DUBOIS (*C. N.*, lxxv., 51).—A study of Sarnstrom's method. Add Fe_2Cl_6 if Fe is low; use large amounts HCl, so as to generate CO_2; large excess carbonate to be avoided. Not reliable for high percentages.

98. BREARLEY (*C. N.*, lxxv., 13).—Acetate separation of Fe; faintly acid filtrate poured into excess of permanganate mixed with $ZnSO_4$ (Wright and Meinecke's modification of Guyard's process, see *J. C. S. Trans.*, 1880), and excess permanganate titrated; or the precipitated MnO_2 may be estimated. Excessive ammonia salts to be avoided (see 109). Describes syphon filter and general corrections for hot aliquot filtrations.

99. SCHÖFFEL and DONATH (*J. C. S.*, lii., 399).—Neutralised with sodium carbonate; add to permanganate and $ZnSO_4$; excess titrated with arsenious acid.

100. DONATH (*C. N.*, xliii., 253; and SCHÖFFEL and DONATH, *J. I. S. I.*, 1883, 381).—Neutral solution of Mn salt flows into hot alkaline permanganate; process ended when supernatant liquid is colourless; Fe present as per-salt does not interfere. Similar process for estimating Cr in presence of Fe and Al.

101. SCHÖFFEL and DONATH (*J. I. S. I.*, 1887, i., 469).—Fe separated with ZnO; without filtration, run into boiling $KMnO_4 + ZnSO_4$—this to avoid formation of lower oxides than MnO_2. Excess permanganate determined with arsenious acid.

102. GIORGIS (*J. I. S. I.*, 1897, ii., 498; and *J. C. S.*, lxxii., ii., 350).—Neutralised solution of Fe and Mn boiled with permanganate and large amounts of soda nitrate; excess permanganate determined. Similar process for Cr if Mn is absent or present in known amount.

103. GHILIAN (*C. N.*, lix., 121).—Titration in presence of ZnO without filtering off Fe. Twenty-five assays in half an hour.

104. BRAND (*J. I. S. I.*, 1887, ii., 368; and 1888, i., 375; REIS, *J. C. S.*, lxiv., ii., 304).—Sample dissolved in nitro-sulphuric acid, oxidised with HNO_3 and barium peroxide, H_2O_2 boiled off, Fe precipitated with ZnO, and solution titrated; precipitate settles rapidly; continuous working with two burettes.

105. RUBRICIUS (*J. I. S. I.*, 1892, ii., 512).—Precipitates Fe with ZnO, and adds $MgSO_4$ previous to titration.

106. JOLLES (*J. C. S.*, lvi., 798).—MnO solution added to faintly alkaline solution of standard manganate until it is decolourised; the precipitate is MnO_2.

Standard Solutions and General Notes.—

107. DUNN (*C. N.*, xlv., 137).—Mixed solutions of $MnSO_4$ and $KMnO_4$ evolve little or no gas in the cold; on heating, O is evolved if the permanganate is in excess.

108. MORSE and REESE (*C. N.*, lxxviii., 77).—Permanganate is reduced and O evolved if MnO_2 is present. To this cause is ascribed the instability of $KMnO_4$ solutions; they should always be carefully filtered.

109. TAMM (*C. N.*, xxv., 26). — Permanganate as an oxidising agent can convert ammonia into HNO_3.

110. MEYER and RECKLINGHAUSEN (*J. C. S.*, lxxii., ii., 19).—H and CO are slowly oxidised by a solution of $KMnO_4$.

111. HARCOURT (*C. N.*, xiii., 293).—Speed of the reaction between permanganate and oxalic acid depends on the relation between permanganate, oxalic acid, manganous sulphate, and sulphuric acid.

112. DYMOND and HUGHES (*J. C. S.*, lxxi., 314).—On titrating H_2SO_3 with $KMnO_4$, only 89 per cent of that required to form H_2SO_4 is used; due to formation of dithionic acid. Same amount formed under varying conditions.

113. LONGI and CAMILLA (*J. C. S.*, lxxii., ii., 387).—MnO_2 adhering to vessel during precipitation due to dirt, and may be prevented by washing with $H_2SO_4 + CrO_3$. Ni, CrO_3, Co, Pb do not interfere with permanganate titration of MnO.

114. LUNGE (*J. C. S.*, xlviii., ii., 62; also *J. C. S.*, lviii., 1469).—Permanganate standardised in acid solution with H_2O_2; evolved O measured. A similar pro-

cess serves to determine available oxygen in pyrolusite, Weldon mud, &c.

115. Morse and Chambers (*J. C. S.*, lxx., ii., 388).—In presence of a neutral reducing agent, such as H_2O_2, permanganate may be standardised with H_2SO_4, or conversely.

116. Riegler (*J. C. S.*, lxx., ii., 676).—Solution of oxalic acid containing large amount of H_2SO_4 keeps unchanged for a year.

117. Lenz (*J. C. S.*, xlviii., 598).—Ten grms. boric acid per litre prevents the decomposition of oxalic acid.

118. Hampe (*C. N.*, xlvii., 260).—Pure dehydrated oxalic acid is obtained by sublimation, and kept over H_2SO_4.

119. McDirby (*C. N.*, xxx., 142). — Permanganate standardised by simply dissolving piano-wire is inaccurate. The small amount of C existing in the Fe is oxidised also, and errors of 1 to 2 per cent are caused. Berthelot has previously drawn attention to this point.

IV.*b. Oxidations to Permanganate.*—

120 Gibbs (*C. N.*, xi., 147).—Has recommended boiling with PbO2 to separate Mn from alkaline earths. A compound, MnO_2+4PbO_2, is formed. [This appears to be the source of error, more or less evident, whenever more than about 0·01 grm. of Mn is boiled in an acid solution with PbO_2.—H. B.].

121. Morse (*J. C. S.*, lxxii., ii., 145). — In presence of HNO_3 the following reaction occurs : — $2HMnO_4+3PbO_2=H_2O+2MnO_2+3PbO+3O_2$.

122. Leclerc (*C. N.*, xxvi., 297) and Pichard (*C. N.*, lxxvii., 108)—Oxidises an acid solution of soils, &c., with red lead; it is necessary to destroy organic matter. Not possible to titrate with $FeSO_4$ on account of $PbSO_4$ (see 136), or oxalic acid on account of $PbCO_3$ (see 134). Titrates with $HgNO_3$, liquid to be freely acid so as to prevent precipitation of Mn oxides (Guyard's reaction).

123. Pechard (*C. N.*, xxvii., 85). — Effects solution by fusing with sodium carbonate. Compares with standard permanganate to 1/10,000 by diluting largely.

124. Deshay (*C. N.*, xxxviii., 70).—Nitric or nitro-sulphuric acid solution of the sample; oxidises with PbO_2. Always the colouration is stronger as the amount of Mn increases. [This is not true when several centigrms. or more Mn is present.—H. B.]. Tone varies according to origin and degree of oxidation. Essential to operate under like conditions. Titrates with soda arsenite.

125. Peters (*C. N.*, xxxiii., 35). — Dissolve in HNO_3; oxidises with PbO_2. Finds 1 per cent to be the limit, using 0·1 grm. of the sample. For spiegels, works on 0·004 grm. Combined carbon does not interfere.

126. Chatard (*C. N.*, xxiv., 196).—Used for dolomite and limestones. Fails for large amounts of Mn. Longer the mixture is boiled more permanganate is there formed, but no limit attainable.

127. Morgan (*C. N.*, lvi., 82).—Oxidation with PbO_2. Colour comparison. Estimates Mn in the sample which has served for colorimetric estimation of carbon.

128. Schlagdenhauffen (*J. C. S.*, xlviii., 442).—Oxidation with PbO_2. Concentration of solution not less than 0·1 per cent Mn or 2 per cent HNO_3. Titrate in very acid solution.

129. Hunt (*J. I. S. I.*, 1886, 1020).—HNO_3 used should be free from Cl or nitrous fumes, and throughout the process should be 1·20 sp. gr.; heats in $CaCl_2$ bath; compares colours. Cheever (*ibid.*) considers the method unreliable.

130. Osmond (*J. I. S. I.*, 1885, 275).—Dissolve in HCl, evaporate; dissolve in HNO_3, add soda metaphosphate and PbO_2. Filtrate compared with standard. The error is 1/50th. PbO_2 may be replaced by current of ozonised oxygen.

131. Rossi (*J. I. S. I.*, 1891, i., 438; and 1892, i., 491).—Like Osmond, but $CaCO_3$ instead of PbO_2. When Cl is evolved the solution is filtered and compared with standard.

132. Moore (*C. N.*, lxiii., 66).—The Mn is oxidised to manganic metaphosphate by means of phosphoric acid and chlorate. The violet liquid is titrated with $FeSO_4$ and $KMnO_4$. Cr is the only metal that interferes.*

134. Thorpe and Hambly (*J. C. S.*, liii., 182).—Oxidation with PbO_2 in nitro-sulphuric solution, and titrate with ammonium oxalate. Not more than 0·01 grm. Mn should be present.

135. Babbit (*J. I. S. I.*, 1887, ii., 369).—Oxidation with PbO_2; supernatant liquid decanted through asbestos, and residue boiled with 20 per cent HNO_3 so long as the decanted liquid is coloured.

136. Weismann (*J. I. S. I.*, 1888, i., 377).—Solution in nitro-sulphuric acid, oxidised with PbO_2, and titrated with $FeSO_4$.

137. Schneider (*J. I. S. I.*, 1892, ii., 512).—As Weismann; titrated with $FeSO_4$ and $KMnO_4$, Cr and Mn may be thus estimated together. Two grms. of sample used.

138. Schneider (*J. C. S.*, lxxiv., ii., 94).—Titration of the permanganate solution with H_2O_2.

139. Schneider (*J. C. S.*, liv., 873.)—Bismuth tetroxide in HNO_3 solution converts Mn to permanganate. Titrate with H_2O_2; Fe or H_2SO_4 have no influence.

140. Reddrop and Ramage (*J. C. S.*, lxvii., 268).—A modification of the previous process in which sodium bismuthate is used instead of the tetroxide. Permanganate filtered into excess H_2O_2 in HNO_3, and titrated back with $KMnO_4$. Cu and Ni are without effect. Cr and Co = 5 per cent cause only slightly high results. Available for any amount of Mn, and completed in fifteen minutes.

141. Van Grundy (*J. I. S. I.*, 1892, ii., 512).—Oxidation with PbO_2, and titration with arsenious acid. Method spoken of as Textors.

142. Koninck (*C. N.*, lix., 230).—Commercial PbO_2 prepared by treating alkaline lead solutions with Cl; this gas carries $MnCl_2$ derived from its preparation. Hence the presence of Mn in PbO_2. (Mn-free red lead easy to obtain.—H. B.).

(To be continued).

ON CITRONELLALIDENECYANACETIC ACID.

By F. TIEMANN.

As the author has already shown (*Berichte*, vol. xxxi., p. 3329), the transformation of citral into citralidenecyanacetic acid, fusible at 122°, serves as an excellent means for identifying and estimating this aldehyde. As the essential oils often contain citronellal as well as citral, it became interesting to examine how citronellal behaved in the presence of cyanacetic acid.

Five grms. of citronellal were well shaken up with a solution of 2·75 grms. of cyanacetic acid and 2 grms. of caustic soda in 20 c.c. of water. It is best to cool the mixture so as to avoid the formation of accessory resinous products. The alkaline solution is exhausted with ether to eliminate all impurities, acidulated, and again exhausted with ether. By evaporating the ether a residue is obtained, which, after a certain time, takes the form of a crystalline mass which can be dried on a porous plate. The return of citronellalidenecyanacetic acid reaches

* This and Nos. 130 and 131 are not oxidations to permanganate; they are classed here, however, because the operations are very similar.

about 40 per cent of the weight of citronellal used. This acid is insoluble in water, easily soluble in alcohol and ether, and crystallises in alcohol or benzene in tablets, fusible at 137—138°. The sodic salt of this acid is specially characteristic; it is relatively very slightly soluble, and separates out in crystals when citronellalidenecyanacetic acid is dissolved, warm, in a not too weak solution of soda, and then allowed to cool. The sodic salt of citralidenacetic acid remains in solution under the same conditions, but the two acids in solution, neutralised with ammonia, are precipitated by chloride of calcium, acetate of copper, and plumbic salts.

The presence of small quantities of citronellal do not interfere with the detection of citral in the form of citralidenecyanacetic acid. In this manner a mixture of 90 parts of citral and 10 parts of citronellal treated with cyanacetic acid gives a large quantity of a solid product, which, re-crystallised in a mixture of benzene and ligroin, appears in the form of characteristic crystals fusible at 122°.—*Berichte*, 1899, p. 824.

ON THE SEPARATION AND DETERMINATION OF ARSENIC AND ANTIMONY IN ORES.*

By O. C. BECK and H. FISHER.

THIS work was undertaken with the idea of comparing the different known methods, and determining which was the shortest and at the same time the most accurate.

The ore used was an artificial mixture of a native oxide of antimony and a mispickel.

Decomposition of the Ore.

1. This was effected by treating with hydrochloric, nitric, and tartaric acids ("Cairn's Quantitative Analysis, 3rd edition, p. 232); any residue remaining was leached with ammonium polysulphide. The solution was then diluted, and the arsenic and antimony precipitated with hydrogen sulphide. These sulphides were then dissolved in hydrochloric acid and potassium chlorate, and the arsenic and antimony separated by either of the methods which will be given in that section.

2. *Decomposition by means of Caustic Soda* (H. Rose, "Fresenius's Quantitative Analysis, 10th Am. Ed., p. 572). About 5 grms. ore was fused with approximately eight times its weight of sodium hydrate, with a little sodium carbonate and nitrate in an iron dish until completely decomposed. The fusion was allowed to cool and then leached with boiling water and allowed to stand for twenty-four hours with one-third its volume of alcohol. The solution was then filtered and the residue washed, first with alcohol diluted with twice its volume of water, then with a mixture of equal volumes, and finally with a mixture of three volumes of alcohol to one volume of water. To each of these alcoholic solutions a few drops of sodium carbonate solution was added. This treatment converts the arsenic and antimony respectively into soluble sodium arsenate and insoluble sodium metantimonate.

3. *Decomposition by means of Sulphur and Sodium Carbonate* (H. Rose, "Cairn's Quantitative Analysis," 3rd edition, p. 232).—About 0·5 grm. ore was fused with three parts of sodium potassium carbonate and three parts of sulphur, the melt leached with hot water, and filtered from the insoluble residue. This gives the soluble sulpharsenate and sulphantimonate from which the arsenic and antimony are precipitated by acidifying with dilute sulphuric acid. This precipitate was dissolved in hydrochloric acid and potassium chlorate, and the arsenic and antimony separated.

4. *Decomposition by Hydrochloric Acid and Potassium Chlorate* (Pattinson, *Journal Society of Chemical Industry*, vol. xvii., p. 211; and Fischer, *Berichte*, xiii., p. 1778).—From 0·5 to 3 grms. of ore depending upon the amount of arsenic present was dissolved in 30 c.c. concentrated hydrochloric acid and 12 c.c. water, and about five times its weight of potassium chlorate added, heated on the water-bath until the ore was dissolved, and the chlorine driven off. If the potassium chlorate is first placed in the beaker so as to cover the bottom, then the weighed ore placed on this and more chlorate added sufficient to cover the ore and the acid, and water then added, the ore goes into solution more readily than if it is placed directly on the bottom.

5. *Fusion with Sodium Carbonate and Nitrate* (Pearce, CHEMICAL NEWS, vol. xlviii., p. 85).—About 0·35 grm. ore was mixed with about ten times its weight of a mixture of one part sodium carbonate to two parts potassium nitrate in an iron dish, and a cover of the same mixture placed over the whole. The contents were gradually heated to fusion and kept in that state for five minutes. The fused mass was cooled, dissolved in water, digested at a boiling temperature for a few minutes, the residue filtered off and washed. This method was modified as follows:—Instead of fusing the ore directly with the carbonate and nitrate mixture, it was first treated on the water-bath in a porcelain crucible with fuming nitric acid and taken to dryness. This treatment was repeated three times. The mass was then mixed with the carbonate and nitrate and treated as described above.

Another modification of this method was tried. A layer of potassium nitrate was fused on the bottom and sides of the iron dish, and on this the mixture of ore and carbonate and nitrate was placed, and the method carried out as before.

Separation of the Arsenic and Antimony.

1. *Fischer Distillation Method.*—The solution of the ore (see 4) or the sulphides dissolved in hydrochloric acid and potassium chlorate (see 3) was placed in a distilling flask connected with a Liebig condenser, which had a delivery tube dipping into a small amount of water contained in a beaker. About 5 grms. of ferrous sulphate were added, and the contents brought up to 150 c.c. with 30 per cent hydrochloric acid, and distilled till only 35 c.c. of the solution remained. The flask was then cooled, the contents again brought up to 150 c.c. with 30 per cent acid and again distilled. This was repeated till the distillate showed no traces of arsenic when tested with hydrogen sulphide. This required six distillations. The arsenic in the distillate and the antimony remaining in the flask were precipitated with hydrogen sulphide.

2. *Pattinson Method.*—The solution (see 4) was filtered on asbestos, and the residue washed thoroughly with a solution of 30 c.c. hydrochloric acid and 12 c.c. water. The arsenic in the filtrate was then reduced by adding small portions of stannous chloride till the solution was colourless, then a slight excess of the chloride was added. Hydrogen sulphide was then immediately passed into the cold solution till saturated. As long as the solution is so strongly acid that it has a specific gravity of 1·16—1·17 arsenious sulphide precipitates free from the sulphides of lead, cadmium, tin, antimony, and bismuth. The solution is stirred and the precipitate settles rapidly; it is then filtered off, washed with a solution of five parts of concentrated hydrochloric acid to two parts of saturated hydrogen sulphide water, and finally with water alone.

3. *Magnesium Ammonium Arsenate Separation.*—The precipitate of arsenic and antimony sulphides (see 3) was dissolved in hydrochloric acid and potassium chlorate, a small amount of tartaric acid added and ammonium hydrate till nearly alkaline. An excess of magnesia mixture was added, and then about one-third of the volume of alcohol, and the solution finally made alkaline with ammonia. The solution was allowed to stand over night, the precipitated magnesium ammonium arsenate filtered

* Contribution from the Havemeyer Laboratories of Columbia University. From the *School of Mines Quarterly*, vol. xx., No. 4.

off, washed with water containing ammonia till the washings showed no opalescence on acidifying with nitric acid and adding silver nitrate. The filtrate was evaporated to small bulk, acidified with hydrochloric acid, and the antimony precipitated with hydrogen sulphide.

Determination of the Arsenic.

1. *Pearce Method.*—To the filtrate (see 5) nitric acid was added till slightly acid, and the solution boiled to expel carbon dioxide and nitrous fumes. It was then neutralised with zinc oxide. A slight excess of the oxide was added, and the solution allowed to stand over night to remove the last traces of acid. An excess of silver nitrate was added, and the solution again allowed to stand over night to insure the complete precipitation of the arsenic. The precipitate was filtered, washed, dissolved in warm dilute nitric acid, and the solution titrated with standardised ammonium sulphocyanate, using ferric alum as indicator. This titration was made in a 250 c.c. bottle provided with a tightly-fitting glass stopper, as it was found that the precipitate of silver sulphocyanate held some of the silver arsenate, for after the solution showed a permanent red colour after merely shaking; when the bottle was stoppered and well shaken the colour disappeared, and it required another 1/10 c.c. before the red colour was permanent on further shaking.

2. *As Magnesium Ammonium Arsenate.*—The sulphide of arsenic, obtained by both the Fischer and Pattinson methods, was dissolved in fuming nitric acid, the nitrous fumes boiled off, the solution diluted, nearly neutralised with ammonia, cooled, one-third of its volume of 95 per cent alcohol added, and magnesia mixture added slowly with stirring, and a few drops more of ammonia, and the whole allowed to stand over night. The precipitate was then filtered on a Gooch crucible, washed with water containing alcohol and ammonia, dried by gradually heating the crucible over the flame and finally ignited, cooled, and weighed as magnesium pyroarsenate.

3. *As Arsenious Sulphide.*—The precipitated sulphide of arsenic was filtered on a Gooch crucible, washed several times with 95 per cent alcohol, once with absolute alcohol, several times with carbon disulphide, again with alcohol, and finally dried in an air-bath at 110° and weighed.

4. *Titration with Iodine.*—The arsenious sulphide, together with the Gooch crucible, was placed in a beaker with a small amount of concentrated sulphuric acid. The beaker was placed in an air-bath and gradually heated to 140—150°, being left uncovered so as to prevent the deposition of sulphur on the sides. As the sulphide dissolved the solution darkened, and it was heated till the colour disappeared and all sulphur dioxide, which would interfere with the subsequent titration, driven off. The solution was removed from the air-bath, diluted and nearly neutralised with sodium carbonate, then sodium bicarbonate was added till the solution contained a slight excess, then titrated with a standardised N/10 iodine solution, using starch as indicator.

Determination of the Antimony.

1. *As Antimonious Sulphide.*—The antimonious sulphide obtained by (1) or (3) under "separation" was filtered on a weighed Gooch crucible, the precipitate washed with 95 per cent alcohol and then with carbon disulphide. The precipitate was then dried at 200° to constant weight.

2. *As Antimonious Antimonic Oxide.*—The antimonious sulphide was filtered on a Gooch crucible and treated with fuming nitric acid till no more sulphur was visible, when the mass was ignited to drive off the excess of nitric and sulphuric acids. A second method of converting the sulphide to the oxide is (Jannasch, "Practischer Leitfaden der Gerichtsanalyse," p. 145) to filter the sulphide on a small paper, wash with a 5 per cent solution of ammonium nitrate containing hydrogen sulphide. Dry the precipitate, separate it as much as possible from the paper, and place in a small weighed porcelain crucible (50—70 c.c.). Spread the paper on a watch-glass, wash it thoroughly with hot ammonium sulphide, and then with boiling water. Evaporate the solution on a water-bath to dryness, add fuming nitric acid till no more sulphur is visible, then ignite.

3. *Weller Method (Liebig's Annalen*, ccxiii., p. 364).—*Titration of Liberated Iodine.*—The residue obtained by leaching the fusion of Rose's method (see (2) under "decomposition"), which consisted of ferric oxide and sodium hydrogen metantimonate, was dissolved in hydrochloric acid and potassium chlorate. The antimony was then precipitated as sulphide by means of hydrogen sulphide to separate it from the iron and filtered. It was then dissolved in hydrochloric acid and potassium chlorate, and the chlorine and oxides of chlorine driven off by heating on a water-bath or by gently boiling. The solution was diluted to about 200—300 c.c., 5 grms. of potassium iodide added, and the iodine titrated with standard thiosulphate after adding starch solution. The thiosulphate solution used was standardised against copper and calculated to its equivalent in antimony.

4. *Mohr's Method.*—Titration with iodine ("Mohr's Titrirmethode"; and Clarke, *J. S. C. I.*, vol. xv., p. 255). The sodium hydrogen metantimonate obtained by fusion was dissolved in hydrochloric acid and potassium chlorate, the antimony precipitated as sulphide and again dissolved as in the previous method. The antimonic chloride was then reduced to antimonious chloride by means of a sulphurous acid. The excess of acid was then boiled out, 1 to 2 grms. of tartaric acid added, the solution neutralised with sodium carbonate, and 20—30 c.c. of a saturated solution of sodium bicarbonate added, and the solution titrated at a bulk of 200—300 c.c. with standard N/10 iodine, using starch as indicator.

The results obtained by these methods were as follows:—

Arsenic.			
Pearce method	—	15·83	15·94
Pearce method, nitric acid modification	—	16·03	16·17
Pearce method, potassium nitrate modification	—	16·18	16·37
Fischer method	—	16·25	16·38
Pattinson method, iodine titration	—	16·23	16·34
Pattinson method, magnesium pyroarsenate	—	16·23	16·32
Pattinson method, arsenious sulphide	—	16·69	16·94

Antimony.			Jannasch mod.
As antimonious sulphide	18·74	18·91	—
As antimonious antimonic oxide	17·85	17·96	18·02
By Weller method	18·12	18·09	18·16
By Mohr's method	18·31	18·19	18·26

It will be seen from the table that the ordinary Pearce method and the nitric acid modification give slightly low results. This is probably due to a slight loss of arsenic by volatilisation. The potassium nitrate method, while accurate, takes too long.

The Fischer distillation method gives good results, but is also too long.

The Pattinson method is preferable to the other two on account of its accuracy and rapidity, especially when the sulphide is titrated with iodine. When the arsenic is weighed as sulphide the results are high, probably due to the impossibility of completely dissolving the sulphur out of the precipitate.

In regard to the antimony the sulphide also gives high results.

The oxide gave slightly low results due to the unavoidable spattering on treating the sulphide with the nitric acid. Jannasch's modification, while giving slightly higher results, requires a longer time, and introduces a large

amount of sulphur which must all be oxidised before ignition.

The Weller and Mohr methods gave results which agreed closely.

The writers thank Dr. E. H. Miller for his kind assistance throughout this work.

ON A POSSIBLE HYDRIDE OF MAGNESIUM.

(Preliminary Note).

By WM. FRENCH, M.A., F.I.C.

When hydrogen gas, made by the action of cold water on magnesium, is burned, it does so with a very peculiar green flame, and as this has been observed so many times I was led to investigate the cause. The same green colour is observable with the gas obtained by the action of HCl on the metal, but in a lesser degree. Below I give a few preliminary experiments which have been repeated with metal from different sources. Further experiments are now in progress, and Prof. G. D. Liveing, F.R.S., has kindly offered to examine the flame spectroscopically, and compare it with the lines obtained by him when sparking magnesium in hydrogen (*Proc. Roy. Soc.*, 1881).

The gas gives a blackish precipitate with silver nitrate, but in such a small quantity that sufficient has not yet been obtained for an analysis. When the gas is burned at a jet, and a piece of cold porcelain held in it, the flame assumes a beautiful green colour, and with the spectroscope I have by me (which is only a model home-made one) I obtain a green band which looks as if it might be due to magnesium. When the porcelain is not allowed to get too hot a metallic mirror is produced, which very quickly becomes oxidised and white. This again has only been obtained in such small quantities that it has not been fully examined. When the gas is passed through a hot glass tube, on some occasions a deposit has been obtained, and on others I have not been able to get any.

Experiments are in progress to isolate the body, which it seems to me may possibly be a hydride of magnesium.

Grammar School, Bury.

Transformation of Styrolene into Metastyrolene under the Influence of Light.—Georges Lemoine.—Styrolene or cinnamene, C_8H_8, is changed by heat in the dark into a polymer, metastyrolene. This same polymerisation is produced at ordinary temperatures by solar light, but takes place slowly, the mixture remaining homogeneous on account of the metastyrolene dissolving in excess of styrolene. The author's experiments show that in the two cases the part played by the light is that of accelerating an exothermic transformation, which would be produced in darkness at the same temperature, but very much more slowly.—*Comptes Rendus*, vol. cxxix., No. 19.

Dioxide of Molybdenum.—Marcel Guichard.—The author obtains this oxide by two distinct methods: (1) by the action of molybdic anhydride on ammonium molybdate, and (2) by the electrolysis of fused molybdic anhydride. In both cases the oxide obtained was pure and crystallised, analysis showing it to have the formula MoO_2. This research also shows that there is not known another anhydrous oxide of molybdenum, intermediate between the oxides MoO_2 and MoO_3, except that which results from the dehydration of the blue hydrated oxide, if, however, this dehydration can be effected without peroxidation.—*Comptes Rendus*, vol. cxxix., No. 19.

THE VARIATION IN THE COMPOSITION OF "PARIS GREEN," WITH SCHEME FOR ANALYSIS.*

By THOMAS B. STILLMAN, Ph.D.

(Condluded from p. 251).

The chemical examination of pure Paris green is comparatively simple, since it is soluble in slight excess of ammonia, forming a dark blue solution. If it be desired to determine the amount of As_2O_3, a rapid and accurate method is by the use of a standard solution of potassium bichromate, whereby arsenious acid, in acid solution, is oxidised to arsenic acid by the bichromate. The bichromate solution should be of such strength that 1 c.c. of it corresponds to 0·00495 grm. As_2O_3. Full instructions for this method will be found in Sutton's "Volumetric Analysis," p. 138. If arsenic acid is present in the Paris green, its amount can be determined as follows:—Dissolve a sample of the green in dilute hydrochloric acid, pass H_2S gas through the solution until saturated, keeping the temperature of the liquid at about 70° C. Filter, wash the sulphide of arsenic thoroughly with water containing H_2S, transfer precipitate and filter to a flask; add excess of saturated solution of mercuric chloride in HCl (1·12 sp. gr.), and warm until a white precipitate forms, water being added until the volume of HCl in the liquid amounts to about one-sixth. Add excess of standard bichromate solution from a burette, and determine excess over that required to oxidise the arsenious acid by means of standard solution of ferrous sulphate. By this operation the *total* arsenic in the Paris green is determined as As_2O_3. If, now, the amount already existing as As_2O_3 be found and subtracted from the total As_2O_3, the difference should be calculated to As_2O_5—which would be the amount of arsenic acid desired.

The chemical examination of Paris green containing other pigments may or may not be a complex undertaking, depending upon the number of added materials.

The accompanying scheme of analysis, arranged for this purpose, will probably include all varieties of Schweinfurt green.

The following references will be found of service in this connection:—

Manufacture of Paris Green from Scheele's Green by Addition of Acetic Acid (S. Camille Koehlin, *Journ. Soc. Chem. Industry*, v., 596).

Method of Manufacture of Paris Green (Ost, "Technische Chemie," 502).

Estimation of Copper in Paris Green (Böckmann, "Chemisch-Technische Untersuchungsmethoden," ii., p. 195).

Microscopical Examination of Paris Green ("Untersuchungsmethoden," ii., p. 196).

Manufacture of Schweinfurt Green ("Muspratt's Chemistry," vol. i., p. 220).

"Century Dictionary," iii., article relating to green pigments.

Die Mikroskopische Untersuchung des Schweinfurter Grüns und seine Bildung (Sattler, *Zeit. Anal. Chem.*, 2 S., 35).

Le vert de Schweinfurt (Köehlin, *Bull. Mulhouse*, 56 S., 444).

Das Schweinfurter Grün und seine Schicksale (Koller, *Gew. Zeit.*, 49 S., 102; *Ind. Zeit.*, 25 S., 265).

Prüfung arsenhaltiger Farben und Tapeten (Reichardt, *Apoth. Zeit.*, 4 S. 226).

From *The Stevens Indicator*, vol. xv., No. 3.

SCHEME FOR ANALYSIS OF "PARIS GREEN"

CONTAINING

$BaSO_4$, $PbSO_4$, $3CuOAsO_3Cu(C_2H_3O_2)_2$, $PbCrO_4$, ZnO, and $CaCO_3$.

Add excess of dilute nitric acid, warm, filter, and wash well with hot water.

Residue { $BaSO_4$, $PbSO_4$.

Transfer to a No. 3 beaker, add excess of a saturated solution of ammonic acetate; warm ten minutes, filter, wash with hot water.

Residue, $BaSO_4$.

Dry, ignite, and weigh as $BaSO_4$.

$BaSO_4$.

Solution.

Add excess of dilute H_2SO_4, evaporate to dryness; add dilute H_2SO_4, warm, filter, wash with hot water, dry, ignite, and weigh as $PbSO_4$.

$PbSO_4$.

Solution.—Add slight excess of dilute H_2SO_4, evaporate nearly to dryness, allow to cool, add dilute H_2SO_4, warm, filter, and wash well with water.

Residue, $PbSO_4$.

Dry, ignite, and weigh as $PbSO_4$, and calculate to $PbCrO_4$.

$PbCrO_4$.

Solution.—Pass H_2S gas through the liquid to saturation, keeping the temperature of the solution at about 70° C. Filter, wash with water containing H_2S.

Residue, CuS As_2S_3.

Transfer to a No. 3 beaker, add excess of strong solution of sodium sulphide, warm gently ten minutes, filter, wash with water.

Residue, CuS.

Dissolve in nitric acid, dilute with water, filter off any separated sulphur, and determine copper by electrolysis. (See "Stillman's Engineering Chemistry," p. 5).

Cu.

Solution.

Acidify with HCl, pass H_2S gas to saturation, filter, wash with H_2S water, and determine arsenic by method of Kessler. (See "Sutton's Volumetric Analysis," p. 138).

As_2O_3.

Solution.—Boil to expel the H_2S, make alkaline with ammonic hydrate (*a*), warm, filter, wash well with hot water.

Residue, $Cr_2(OH)_6$.

Dry, ignite, and weigh as Cr_2O_3. Calculate to—

$PbCrO_4$.

This weight should equal the weight of $PbCrO_4$ found by determination of the lead in Column 3.

$PbCrO_4$.

Solution.—Pass H_2S gas to saturation, filter, wash with water containing a few drops of ammonic sulphide.

Residue, ZnS.

Dissolve precipitate in HCl, dilute with water, boil, add gradually slight excess of sodium carbonate; boil three minutes, filter, wash thoroughly with hot water, dry, ignite, and weigh as ZnO.

ZnO.

Solution.

Boil to expel the H_2S, add a few drops of ammonic hydrate, then excess of solution of ammonic oxalate. Set aside two hours, filter, wash with water containing $\frac{1}{10}$ volume of ammonic hydrate, dry, ignite, and weigh as CaO, and calculate to $CaCO_3$.

$CaCO_3$.

(*a*) If a white precipitate forms, of zinc hydroxide, add ammonic hydrate until it dissolves. If it be desired to determine the acetic acid, another portion of the Paris green should be taken, and tested by C. Mohr's process. (Consult page 82, "Sutton's Volumetric Analysis").

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 2nd, 1899.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

(Concluded from p. 254).

132. "*Notes on Polyazo-compounds.*" By RAPHAEL MELDOLA and WILLIAM ARTHUR WILLIAMS.

Paranitrobenzene azophenol (Meldola, *Trans.*, 1885, xlvii., 658) melts at 213—216° if the temperature of the bath is raised rapidly. The melting-point formerly given (184°) is erroneous, and the error has been corrected in the latest edition of Beilstein (vol. iv., p. 1410). The compound has been further characterised by its benzoyl and acetyl derivatives: — p-$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}C_6H_5$; slender, orange needles, m. p. 195°.

$$p\text{-}NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_3;$$

dull, orange needles, m. p. 147°. The corresponding amidobenzeazophenol melts at 186° (181° in original description), and forms a difficultly soluble sulphate crystallising in silvery scales having the formula $(p\text{-}NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH)_2,H_2SO_4+3H_2O$.

The base, on acetylation with acetic anhydride and sodium acetate, gives a mixture of a diacetyl with a monacetyl derivative, the latter being phenolic in character: $C_2H_3O{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$; minute, dull orange needles, m.p. 203°; $C_2H_3O{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}O{\cdot}C_2H_3O$; bright, orange scales, m.p. 236—237°.

The disazo-compound, $C_6H_4(N_2{\cdot}C_6H_4{\cdot}OH)_2$ (Meldola, *loc. cit.*, 659), does not appear to be crystallisable. Boiling with acetic anhydride and dry sodium acetate results in the formation of the diacetyl derivative, $C_6H_4(N_2{\cdot}C_6H_4{\cdot}O{\cdot}C_2H_3O)_2$, which crystallises from nitrobenzene in small golden-yellow plates melting at 246—248°.

The amidobenzeneazophenol [(m. p. 168°) obtained by Wallach and Schulze (*Ber.*, 1882, xv., 3021) by removing the acetyl group from the corresponding acetamido-compound, is the meta-compound isomeric with our para-compound (m. p. 186°).

Para-amidobenzeneazophenol, when treated at a low temperature with a mixture of dilute sulphuric acid and sodium dichromate, undergoes fission in a remarkable way. The azo-group remains attached to the $NH_2{\cdot}C_6H_4$— residue with the formation of a diazodichromate of the complex $NH_2{\cdot}C_6H_4{\cdot}N_2$— and the simultaneous oxidation of the $C_6H_4{\cdot}OH$ residue to quinone. This mode of decomposition of azo-compounds is being further investigated.

133. "*On Ethyl Dibromobutanetetracarboxylate and the Synthesis of Tetrahydrofurfuran-aa'-dicarboxylic Acid.*" By BEVAN LEAN, D.Sc., B,A.

A solution of ethyl butanetetracarboxylate in chloroform is readily acted on by bromine with the formation of *ethyl-aa'-dibromobutanetetracarboxylate*,—

$$\begin{array}{l} CH_2{\cdot}CBr(CO_2Et)_2 \\ | \\ CH_2{\cdot}CBr(CO_2Et)_2 \end{array}.$$

The crystalline dibromo-compound (m. p. 83°) thus obtained, when digested for some hours with a strong solution of barium hydroxide, yields an insoluble barium salt of dihydroxybutanetetracarboxylic acid,—

$$Ba(O_2C)_2C(OH){\cdot}CH_2{\cdot}CH_2{\cdot}C(OH)(CO_2)_2Ba,H_2O.$$

If this salt is decomposed by sulphuric acid, there results a solution of *dihydroxybutanetetracarboxylic acid*,—

$$(HO_2C)_2C(OH){\cdot}CH_2{\cdot}CH_2{\cdot}C(OH)(CO_2H)_2.$$

On slowly concentrating the very acrid aqueous solution of this substance over strong sulphuric acid, long needles were obtained of the *monolactone*,—

$$\begin{array}{l} (HO_2C)_2C{\cdot}CH_2{\cdot}CH_2{\cdot}C(OH){\cdot}CO_2H \\ \quad | \qquad\qquad\qquad | \\ \quad O\text{———}CO \end{array}.$$

The silver salt of this substance ($C_8H_8O_9$) was prepared and has the composition $C_8H_6Ag_4O_{10}$. The substance, therefore, readily takes up again the elements of water, as is customary with δ-lactones. It begins to soften at 145°, and at 156° fusion is complete and carbon dioxide is evolved.

On heating an aqueous solution of this lactone in a sealed tube at 150°, the acid is decomposed with elimination of carbon dioxide. If the aqueous solution be evaporated to a small bulk and placed over sulphuric acid, small star-shaped clusters of crystals gradually appear, and eventually the whole becomes solid. The product is found to have the composition $C_6H_8O_5$, which is that of dihydroxyadipic acid less one molecule of water, and the simplest explanation would be that the substance is the δ-lactone of dihydroxyadipic acid, viz.,—

$$\begin{array}{l} CO_2H{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH) \\ \quad | \qquad\qquad\qquad | \\ \quad O\text{———}CO \end{array}.$$

But careful examination shows that this is not so, for the silver salt was prepared and found to have the composition $C_6H_6Ag_2O_5$. Further investigation shows that the elimination of water takes place between the two hydroxyl-groups, and that the substance is *tetrahydrofurfuran-aa'-dicarboxylic acid*, formed thus:—

$$\begin{array}{l} CH_2{\cdot}CH_2 \\ | \quad | \\ HO_2C{\cdot}C \quad C{\cdot}CO_2H \\ | \quad | \\ HO \quad OH \end{array} = \begin{array}{l} CH_2{\cdot}CH_2 \\ | \quad | \\ HO_2C{\cdot}C \quad C{\cdot}CO_2H \\ \quad \diagdown \quad \diagup \\ \quad\quad O \end{array} + H_2O.$$

This substance begins to melt at 65°, but fusion proceeds only gradually, and is not complete till about 120°. The absence of a definite melting-point pointed to it being a mixture of stereoisomeric acids, and experiments were made to separate them by fractional crystallisation from water.

A higher melting *tetrahydrofurfuran aa'-dicarboxylic acid*, ($C_6H_8O_5$), m. p. 123—125°, was isolated, and also crystals melting at 63—64°, which had the composition $C_6H_{10}O_6$. This latter substance was at first supposed to be dihyproxyadipic acid, but the silver salt was prepared and found to be $C_6H_6Ag_2O_5$, a result which led to the conclusion that the substance was the isomeric *monohydrate of tetrahydrofurfurandicarboxylic acid*.

When the substance $C_6H_{10}O_6$ (m. p. 63—64°) was placed for some days over strong sulphuric acid, the product melted at 93—25°, and it then had the composition $C_6H_8O_5$. Its silver salt was $C_6H_6Ag_2O_5$, confirming the conclusion that the substance $C_6H_8O_5$ (m. p. 93—95°) was a lower melting *tetrahydrofurfuran-aa'-dicarboxylic acid*. It reverts to the monohydrate when exposed in the air.

This case of geometrical isomerism would appear to be the first one established in the furfuran series.

The author also discusses and criticises F. Tiemann's work on isosaccharic acid and "norisosaccharic acid," and shows that all the derivatives of these two acids which he has described are probably derivatives of $\beta\beta'$-dihydroxytetrahydrofurfuran-$a a'$-dicarboxylic acid.

134. "*The Application of Powerful Optically Active Acids to the Re-solution of Externally Compensated Basic Substances. Re-solution of Tetrahydroquinaldine.*" By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

In continuation of previous work (*Proc.*, 1899, xv., 124) the authors find that dextrotetrahydroquinaldine cannot be prepared in quantity in a pure condition from the dextrocamphor sulphonate nor the hydrochloride of the crude dextro-base obtained from the inactive base; the benzoyl-derivative of the dextro-base can be easily isolated from the crude dextro-base, and on hydrolysis with hydrochloric acid yields the dextro-base in a pure state.

The following molecular rotations, determined in dilute aqueous solution, are closely related in that the values for the first two salts can be calculated directly from those of the third and fourth:—

Dextrotetrahydroquinaldine dextrocamphorsulphonate, $[M]_D = +173{\cdot}3°$.
Lævotetrahydroquinaldine dextrocamphorsulphonate, $[M]_D = -69{\cdot}5°$.
Lævotetrahydroquinaldine hydrochloride, $[M]_D = -121{\cdot}7°$.
Ammonium dextrocamphorsulphonate, $[M]_D = +51{\cdot}7°$.

135. "*The Application of Powerful Optically Active Acids to the Re-solution of Feebly Basic Substances. Re-solution of Camphoroxime.*" By William Jackson Pope.

The only basic substances hitherto resolved into optically active compounds by crystallisation with an optically active acid have been powerful bases, because feeble bases do not form stable salts with tartaric acid. By using a poweful optically active acid, however, feebly basic externally compensated substances, such as oximes, may be resolved. Thus by fractionally crystallising a mixture of racemic camphoroxime with Reychler's dextrocamphorsulphonic acid from a solution in acetone or ether, the isomeric salts, *dextrocamphoroxime dextrocamphorsulphonate* and *lævocamphoroxime dextrocamphorsulphonate*, $C_{10}H_{16}NOH,C_{10}H_{15}OSO_3H,H_2O$, may be isolated; the former has the specific rotation $[\alpha]_D = +4{\cdot}3°$, whilst the latter gives $[\alpha]_D = +41{\cdot}7°$. Both salts are decomposed by water, yielding the corresponding optically active camphoroximes.

136. "*The Application of Powerful Optically Active Acids to the Re-solution of Externally Compensated Basic Substances. Re-solution of Tetrahydroparatoluquinaldine.*" By William Jackson Pope and Edmund Milton Rich.

In continuation of previous work (*Proc.*, 1899, xv., 171) the authors have isolated *dextrotetrahydroparatoluquinaldine* as its hydrochloride from the mother-liquors remaining after separating the lævo-isomeride as dextrobromocamphorsulphonate from the externally compensated base; the *hydrochloride* of the new base crystallises in sphenoidally hemihedral orthorhombic crystals containing one molecule of water. The optically active bases themselves crystallise from light petroleum solutions in hemimorphic monosymmetric prisms.

137. "*Homogeneity of Dextrolævo-α-phenethylamine Dextrocamphorsulphonate.*" By William Jackson Pope and Alfred William Harvey.

Externally compensated α-phenethylamine combines with Reychler's dextrocamphorsulphonic acid, yielding *dextrolævo-α-phenethylamine dextrocamphorsulphonate*, $CH_3{\cdot}CH(Ph){\cdot}NH_2,C_{10}H_{15}OSO_3H$, which crystallises from acetone in minute colourless prisms melting at 141—143°. The salt has the molecular rotation $[M]_D = +51{\cdot}5°$ in dilute aqueous solution, and since ammonium dextrocamphorsulphonate gives $[M]_D = +51{\cdot}7°$ in aqueous solution, the new salt belongs to the class of partially racemic substances discovered by Ladenburg. Externally compensated *α-phenethylamine platinochloride*, $(CH_3{\cdot}CHPh{\cdot}NH_2)_2,H_2PtCl_6$, crystallises in golden-yellow scales melting at 213—214°.

138. "*The Characterisation of Racemic Liquids.*" By Frederic Stanley Kipping and William Jackson Pope.

It is shown that the results obtained by Ladenburg's latest method (*Ber.*, 1899, xxxii., 1822) for discriminating between "racemic" and "non-racemic" liquids have no bearing upon the question they are supposed to answer.

Series of experiments have further been made to determine the equilibrium between mixtures of dextro- and lævo-pinene in various proportions and their solutions in ethyl and methyl alcohol. It is shown that the distribution ratio of the excess of one antipodes over the other in the oil and in the alcoholic solution in contact with it is nearly independent of the concentration of that excess. This behaviour is explained by Nernst's distribution law, and would be expected with both racemic and non-racemic substances.

Experiments with dextro- and lævo-camphorsulphonic chlorides are also described, which show the fallacious nature of the conclusions drawn by the application of Ladenburg's method.

139. "*A Method for discriminating between 'Non-racemic' and 'Racemic' Liquids.*" By William Jackson Pope and Stanley John Peachey.

The densities of lævo- and externally compensated tetrahydroquinaldine are the same under similar conditions, namely, $d_{t_4}^{\circ} = 1{\cdot}01930 + 0{\cdot}00079\ (20 - t)$ between 14° and 21°; their molecular refractions are also the same, the observed values being—

$$\mathfrak{M}_D = 47{\cdot}50$$

for the active, and—

$$\mathfrak{M}_D = 47{\cdot}57$$

for the inactive base. These numbers afford no evidence that the inactive liquid base is racemic.

The variations in specific rotation of non-electrolytes dissolved in various solvents are traced, in the main, to variations in the association factor of the dissolved substance, and it is shown that the highly associated lævotetrahydroquinaldine has specific rotations varying from $[\alpha]_D = -46°$ to $-118°$ in different solvents. On dissolving the base in solvents having nearly its own association factor, such as tetrahydroquinoline, the specific rotation of the active base remains nearly the same as in the solvent free-state, because its association factor remains nearly unchanged; lævotetrahydroquinaldine, when dissolved in the externally compensated base as solvent, has practically the same specific rotation as in the pure liquid state, namely, $[\alpha]_D = -58{\cdot}12°$. It follows that externally compensated tetrahydroquinaldine has the same molecular weight in the liquid state as its active components, and consequently cannot be a racemic compound.

It is shown that the specific rotation of lævopinene, an unassociated liquid, changes comparatively slightly with the solvent, and that it has the same specific rotation when dissolved in the externally compensated hydrocarbon as when in the pure liquid state. Inactive pinene is therefore not racemic.

The authors conclude that the above results afford the first method for discriminating between racemic and non-racemic liquids which has yielded positive results.

140. "*On Two Hydrated Cobalt Oxides, Green- and Buff-coloured.*" By W. N. Hartley, F.R.S.

The preparation and analysis of two hydrated cobalt oxides is described. The green compound was formed when a cold solution of cobalt chloride was precipitated by an equivalent quantity of barium hydroxide, both solutions having been boiled, and a Torricellian vacuum being maintained in the precipitating vessels. Its formula is $Co_3O_4,6H_2O$. The buff-coloured compound resulted when the precipitation was carried out in like manner, but with excess of barium hydroxide. Its composition is $Co_8O_9,11H_2O$.

The action of acetic acid on the green hydrate separates a brown oxide already known as Co_3O_4. There was a similar action and the separation of black oxide from the buff-coloured hydrate. This points to the following formulæ:—Green hydrate, $Co_2O_3,Co(OH)_2,5H_2O$. Buff hydrate, $Co_2O_3,6Co(OH)_2,5H_2O$. These are distinct compounds, and not merely mixtures.

141. "*A Method of Separating Isomeric Xylidines from the Commercial Product.*" By W. R. Hodgkinson and L. Limpach.

This method depends on the fact that acetate of meta-(Me : Me : NH_2 = 1 : 3 : 4)-xylidine crystallises very readily when the crude mixture is treated with acetic acid. From the filtrate from this acetate, hydrogen chloride precipitates the para-(Me : NH_2 : Me = 1 : 2 : 4)-xylidine as hydro-

chloride, and the filtrates from this, on concentration and heating, yields up the hydrochloride of the (Me:NH.:Me = 1:2:3)-xylidine as a crystalline sublimate. The residue of hydrochlorides of the two ortho-(Me:Me:NH_2 = 1:2:3) and (Me:Me:NH_2 = 1:2:4)-xylidines is hydrolysed and the bases converted into formyl derivatives; that from the (Me:Me:NH_2 = 1:2:3)-base crystallises moderately easily, whilst the other from the (Me:Me:NH_2 = 1:2:4) base is exceedingly difficult to obtain as a solid.

142. "*Action of Hydrolytic Agents on α-Dibromocamphor, and the Constitution of Bromocamphorenic Acid.*" By ARTHUR LAPWORTH.

In addition to the experiments already briefly described (*Proc.*, 1899, xv., 161), the paper gives an account of the behaviour of α-dibromocamphor towards hydrolytic agents other than moist silver compounds. It is found that this substance is readily attacked by mercurous nitrate dissolved in boiling acetic acid, and that a small quantity of bromocamphorenic acid is obtained. It is not attacked by lead compounds under these conditions, and chars when heated with water and lead oxide in closed tubes to 120—150°; in the latter case, no bromocamphorenic acid could be detected, but a small quantity of camphoric acid, and in one instance a minute quantity of camphorquinone, was found to be produced.

The action of oxidising agents on dibromocampholid, bromocamphorenic acid, α-monobromocampholid, and other derivatives of camphorenic acid has been investigated. It is found that in each case where oxidation occurs nearly pure homocamphoronic acid is obtained, an excellent yield of the latter substance being produced when α-monobromocampholid is oxidised with dilute nitric acid and silver nitrate.

PHYSICAL SOCIETY.

Ordinary Meeting, November 24th, 1899.

Prof. G. CAREY FOSTER, F.R.S., Vice-President, in the Chair.

A PAPER "*On the Conductivities of certain Heterogeneous Media for a Steady Flux having a Potential*" was read by Dr. C. H. LEES.

Two formulæ have already been proposed to express the conductivity of a mixture in terms of the conductivities of its constituents. In the first formula the conductivity is represented as the sum of a number of terms each one of which is the product of the conductivity of any constituent and the fractional part of the mixture which is made up of that constituent. In the second formula the resistivity of a mixture is expressed in the same way with respect to the resistivities and percentages of its constituents. In general the first of these suppositions gives results which are above the experimental values, while the second gives results which are below. If we suppose that the mixture is made up of a series of columns of the separate parts stretching normally between two equipotential surfaces, then the conductivity would be accurately represented by the first formula. If, however, we assume that the constituents are arranged in parallel layers, then the second formula would apply. In the present paper the author has attacked the problem two-dimensionally, and has investigated the relation which holds between the conductivities when the constituents are arranged in the mixture alternately, like the squares on a draught-board. Dealing first with two components, it is easily shown that the problem reduces itself to finding the form of the equipotential curves and of the stream lines in a square which is divided by a diagonal into two parts of different material. By means of conformal representation, Dr. Lees has referred the square under consideration to a kite-shaped quadrilateral with two opposite angles right angles, and the other two so determined by the conductivities of the constituents as to give straight equipotential lines in the two portions of the figure which represent the two materials, and which are separated the one from the other by the axis of symmetry. The general relation which exists between the vector co-ordinates in the two systems has been proved by Love to consist of elliptic functions, but near the angular points of the figures a close approximation can be obtained by the use of a simple exponential expression. Taking the known solution to the problem in the case of the kite-shaped quadrilateral, it is easy to calculate the result for the square under consideration. This leads to the conclusion that the conductivity of the square is the geometric mean of the conductivities of the constituents. Allowing the medium to become fine-grained, and introducing new materials, it follows at once that the logarithm of the conductivity of a mixture is equal to the sum of a number of terms, each one of which is the product of the logarithm of the conductivity of any constituent and the fractional part of the mixture which is made up of that constituent. By a superposition of fluxes the author has shown that the above law holds for flows in four directions, and he therefore considers that with the assumed structure the formula represents the conductivity for any flux.

Dr. LEES then read a second paper, "*On the Thermal Conductivities of Mixtures and their Constituents.*"

In this paper the three formulæ considered in the preceding communication are applied to the known experimental results upon the conductivities of mixtures of liquids. The author finds that the least satisfactory formulæ is the first one, whereas the least unsatisfactory is the logarithmic one.

Mr. APPLEYARD said that it was frequently of importance to be able to determine the resistance of a mixture of gutta-perchas from the known resistances of component parts. He had attempted, without success, to do this by means of the old formulæ, and he would be interested to see whether Dr. Lees' logarithmic formula gave better results. In electrical work Mr. Appleyard pointed out that the nature of the contacts affected the conductivity, the resistance of a sheet of rubber being different when measured between metal plates and mercury sheets.

Mr. CAMPBELL said that the difference between the calculated and observed results might be due to the thermo-electric properties of the materials. Lord Rayleigh had observed that the high resistivity of alloys might be due to a back E.M.F. produced by the contact of dissimilar metals. Mr. Campbell said that he had measured the resistances of ferro-nickels both with direct and alternative currents, and found them the same in the two cases.

In reply, Dr. LEES said that all his experimental work on conductivity had been carried out with mercury contacts.

The Society then adjourned until December 8th, when, by the invitation of Prof. S. P. Thompson, the Meeting will be held in the Physical Laboratory of the Finsbury Technical College.

CORRESPONDENCE.

THE PERIODICITY OF MELTING- AND BOILING-POINTS.

To the Editor of the Chemical News.

SIR,—With every new property of a body which can in any way help the establishment of the Periodic Law, there always arises the question of the periodicity of melting- and boiling-points.

One fact seems to have always been neglected in discussing this point. When we speak of the melting- or boiling-point of an element or compound, we always measure from some arbitrary zero. For instance, water boils at 100° C., and mercury at 360° C.; that is, 100°

Compound.	M.-p.	B.-p. (at 15 m.m.).	B.-p.—M.-p.			Difference.
$C_{20}H_{42}$ ..	36·7	205	168·3			
						6·3
$C_{21}H_{44}$ ..	40·4	215	174·6			
						5·5
$C_{22}H_{46}$ ..	44·4	224·5	180·1			
						6·2
$C_{23}H_{48}$ ..	47·7	234	186·3			
						5·6
$C_{24}H_{50}$ ..	51·1	243	191·9			
				5·86		
$C_{25}H_{52}$ ..				5·86	17·58	18·6
$C_{26}H_{54}$ ..				5·86		
$C_{27}H_{56}$ ..	59·5	270	210·5			
				5·86		
$C_{28}H_{58}$ ..				5·86		
$C_{29}H_{60}$ ..				5·86	22·44	24·4
$C_{30}H_{62}$ ..				5·86		
$C_{31}H_{64}$ ..	68·1	302	234·9			
						5·1
$C_{32}H_{66}$ ..	70	310	240	5·86		
$C_{33}H_{68}$ ..				5·86	17·58	
$C_{34}H_{70}$ ..				5·86		16·3
$C_{35}H_{72}$ ..	74·7	331	256·3			
And—		At 760 m.m.				
$C_{17}H_{36}$ ..	22·5	303	270·5			
						8·5
$C_{18}H_{38}$ ..	28	317	279			
						9
$C_{19}H_{40}$ ..	32	330	298			

and 360° above o, this particular zero being the melting-point of water. But this temperature o° C. does not treat mercury in the same way as it treats water. At o° C., water is in a condition corresponding to that of mercury at −9° C. In the history of chemistry there has been a case analogous to this, namely in the "law of Dulong and Petit," where carbon, boron, and silicon did not give the same atomic heat as the other elements until the specific heat was taken in each case at a temperature approximately similarly distant from its melting-point.

So, in the case of melting- and boiling-points, the apparently only fair way of considering the matter is by comparing the number of heat units between the melting- and boiling-points. By this means we get a range of temperature which is similar in each case.

Taking the cases of sodium and potassium, cadmium and mercury, tin and lead, we get—

Element.	M.-p.	B.-p.	B.-p—M.-p.
Na	96·9	818·5	721·6
K	60·2	693	635·5
Cd	320	763·7	443·7
Hg	−9	360	369
Sn	229	1525	1296
Pb	330	1525	1195

Then—

Boiling-point—melting-point (Na ; K :: Cd : Hg :: Sn : Pb)

722 : 636 :: 444 : 369 :: 1296 : 1195

1 : 0·881 :: 1 : 0·831 :: 1 : 0·922

These results seem fairly agreeable, especially as the temperatures are only a rough average of the values found in Landolt's tables.

If the elements above mentioned are, indeed, so to say, corresponding, then—

Atomic weight (Na : K :: Cd : Hg :: Sn : Pb)

should hold good.

23 : 39 :: 118 : 200 :: 119 : 206

1 : 1·7 :: 1 : 1·7 :: 1 : 1·7.

It is, however, a curious thing that sodium and potassium, which are adjacent to each other in Mendeleeff's table, and the two pairs—cadmium and mercury, tin and lead—which are set down as having some other unknown element between them, should have similar atomic weights and similar differences in boiling- and melting-points.

Equally noticeable is the difference in boiling-point—melting-point that an increase or decrease of $-CH_2$ makes in homologous series of organic compounds. (See Table, preceding column).

Seeing that, in taking melting- and boiling-points of organic compounds, discrepancy usually occurs, owing to the different methods of different observers, these numbers may be taken as fairly concordant.

It is evident that the increment for $-CH_3$ might also be found in compounds, or any other group, providing the group is similarly added.

This, then, might be a useful means for checking the constitution of compounds.—I am, &c.,

ALFRED WERTHEIMER.

Laboratory of the Stirling Chemical Works,
Stratford, London, E., Nov. 21, 1899.

DETERMINATION OF CARBON IN IRON AND STEEL WITHOUT ABSORPTION APPARATUS.

To the Editor of the Chemical News.

SIR,—I am not disposed to disagree with Mr. Dougherty if he considers the respective factors given by Schützenberger, Zaboudsky, and Blair to be confirmatory of his own. There are analysts, however, to whom such differences are important, and I had no wish further than to draw their atention to them.

"If the carbonaceous compounds," says Mr. Dougherty, "were soluble in warm dilute nitric acid, how is it that the factor is only 67·5, instead of much higher, in order to compensate for the alleged loss?" Not doubting that Mr. Dougherty had obtained good results, I asked myself a similar question soon after reading his original paper. Zaboudsky observes that the compound is easily nitrated, and it may be suggested, pending a more decisive answer to the question, that, on this account, the carbonaceous residue, when washed with HNO_3, may lose carbon without suffering any diminution in net weight; that it may even increase in weight. Mr. Dougherty will have observed, after washing with hot diilute nitric acid, that the residue changes from black to dark brown, and that the washings reduce very appreciable amounts of permanganate.

Of course the standard combustion process has sources of error to be guarded against. It seems to me, however, that the fact of their being mentioned in some instances is proof of the high degree of accuracy which analysts demand of the process. Respecting what other every-day analytical operation do we hear (if at all) nearly so frequently of the atmospheric influence on the surface of the weighed vessel as we do in relation to the KHO absorption bulb, and what can any one tell us does this amount to in extreme cases? In research work, such as was undertaken by the American Committee in connection with the International Standards, it may be important, but in every day analyses it certainly does not survive, in an appreciable form, the ordinary precautions which are taken to minimise it. Very much the same thing can be said of the other points Mr. Dougherty names, or could

name, which are essential features of the combustion process.

The results Mr. Dougherty quotes towards the end of his letter cannot be taken, and were surely never intended, to indicate the degree of error inherent in the combustion process. If they are to be discussed, without misunderstanding, then we must be assured that accidental errors and irregularities in the sample which your correspondent says "are bound to occur occasionally" have been *certainly* eliminated. This point must be the more strongly insisted on as the sample appears to have been a pig-iron containing graphite, and in that case accurate sampling from a heap of drillings is purely fortuitous. Moreover, the combined carbon, being determined by subtracting the graphite from the total carbon, shows all errors, due to more or less of the powdery graphite being taken with the sample, in the percentage of combined carbon.

With samples identical in composition such results (varying from 0·29 to 0·91 per cent) *could not* be obtained. There is the less hesitation in this statement because, during the past few years, I have personally made over five thousand such combustions, and, no matter what foreign element happened to exist in the steel, I have found the process worthy of every confidence.—I am, &c.,

Harry Brearley.

Totley, near Sheffield.

THE NEWLY-DISCOVERED GASES.

To the Editor of the Chemical News.

Sir,—In a note of mine on Argon, dated March 15th, 1895, in the Chemical News (vol. lxxi., p. 140), an endeavour was made to show that the four metalloid series in the periodic system point to the existence of four elements of no valency of atomic weights, 20, 37, 82, and 129 respectively.

It was further remarked that the metal series also point just as strongly to the same four inactive elements in addition to others, amongst which is one of atomic weight 5.

In this connection it may be worth while to note that in an Address on "The Newly-discovered Gases" to the conference of German men of science at Munich in September last, Dr. Ramsay gave the atomic weights of the newly-discovered gases as follows (see *Nature*, vol. lxi., p. 62), viz:—

Helium	4
Neon..	20
Argon	40
Krypton	82
Xenon	128

If the two sets of values are placed side by side, as in the following table, the facts speak for themselves:—

Calculated values	5	20	37	82	129
Observed values	4	20	40	82	128

—I am, &c.,

W. Sedgwick, Lt.-Col., late R.E.

November 28, 1899.

TESTING OIL OF TURPENTINE.

To the Editor of the Chemical News.

Sir,—In commerce oil of turpentine is often replaced by "turpentine substitute," *i.e.*, benzine, or a mixture of benzine, petroleum oil, and turpentine. An easy method of detecting the benzene, or other substances having a lower boiling-point than turpentine, is by the use of the tube described as follows:—

A piece of ¼ inch bore glass tubing 8 inches long has a bulb blown on one end; about 4 inches from this and in the length of the tube another bulb is blown; the tube between the bulbs is then heated and bent until the bulbs are opposite each other; we thus obtain a tube with a short closed leg and a longer open leg. The turpentine to be tested is poured into the tube, and by a bit of manipulation the closed end of the tube can be completely filled; mercury is then poured into the tube, and by carefully working the matter the mercury can be made to partially fill the bulb on the closed end of the tube, and retain a small quantity of the liquid without an air bubble being present; mercury is then poured in until the level in the open leg of the tube is nearly equal to that in the closed leg. The tube is now placed in an oil-bath and heated; if the turpentine is pure there will be no motion of the mercury until a temperature of 156° C. is reached, but if benzine be present the mercury will rise in the longer leg of the tube when the temperature reaches about 148° C. In fact, if the turpentine contains any substance with a boiling-point lower than that of pure turpentine, it will be shown by the mercury being set in motion before a temperature of 156° C. is reached.—I am, &c.,

W. A. Bradbury.

LABORATORY LAMP.

To the Editor of the Chemical News.

Sir,—"Chemicus" asks in your last issue for a lamp which will take the place of a Bunsen burner in laboratories where coal-gas is not obtainable. In one of the council's laboratories we have recently had to meet this requirement, and have obtained from the apparatus sellers a Bunsen burner, which is fed with methylated spirit from a reservoir at higher level. The spirit is converted into vapour in the lower part of the burner by the heated metal of the burner itself, and becomes mixed with air automatically in the usual way. The flame which is produced by burning this mixture is easily regulated, and is preferred to the coal-gas flame by those who are working with it. It is cleanly, hot, and inexpensive.—I am, &c.,

Frank Clowes.

Adsorption Test of Cadmium in presence of Copper.—Trey (*Zeit. Anal. Chemie*, xxxvii., 743). The solution received the addition of ammonia until it showed the blue colouration (presumably to re-solution of the light bluish precipitate). A drop of this solution was then allowed to wet the centre of a disc of filter-paper. In extending by capillary action Cd salt will extend outside of the part wetted by the Cu (adsorption) and testing with $(NH_4)_2S$ shows a yellow ring surrounding the brown spot due to CuS. The author devised a simple apparatus for making these tests consisting of a piece of ordinary tubing bent in U form with one end expanded to funnel shape, the other end drawn down to a fine jet, the whole set in a large flat cork, with a small wire frame to support the filter-paper which is to be laid over the jet.—*School of Mines Quarterly.*

Determining Alkaline Earths in presence of one another without previous Separation.—Knobloch (*Zeit. Anal. Chem.*, xxxvii., 734).—After qualitative tests to determine whether one, two, or all three (Ca, Sr, Ba) are present, the earths are precipitated as carbonates, and weighed as such. The filter-paper being ignited separately, and the whole treated with $(NH_4)_2CO_3$ and heated carefully at a temperature insufficient to causticise (below red heat). Then about 8 grms. of strictly C.P. borax is heated in a platinum crucible at the full heat of a Bunsen burner for two hours, cooled, and weighed. To this is then added the alkaline earth carbonates, and heat is applied carefully at first until the effervescence of CO_2 has practically ceased, when a strong heat is applied for an hour, the crucible being surrounded by a clay chimney. After cooling, the increase in weight is due to the oxides. Knowing the weight as carbonates and as oxides, the respective amounts can be calculated easily when but two are present. In case all three are present, the Ba is separated out by K_2CrO_4 in a solution slightly acid with acetic. —*School of Mines Quarterly.*

NOTICES OF BOOKS.

Tables for Quantitative Metallurgical Analysis for Laboratory Use. By J. James Morgan, F.C.S. London: C. Griffin and Co. 1899. 16 tables.

The information given in this book will considerably lighten the labours of the metallurgical chemist, inasmuch as a large amount of detail work has been concentrated and tabulated in the familiar and useful form of analytical tables. The method of division into groups has been adopted as far as possible, and a method of analysing one member, printed in large type, is described, which, with modifications, can be easily applied to other members of the same group. The whole is admirably arranged, but we must take exception to the binding; each sheet appears to be glued to a backing, and though the book opens *flat* at any place it speedily comes to pieces.

Science Data Diary. Philip Harris and Co., Birmingham. 1899.

This handy little pocket-book contains, in a very compact form, a large number of tables, &c., of use to the chemist, engineer, and electrician. If there is a fault to be found it is that some sheets are printed in such small type as to be almost illegible.

There is also a renewable calendar and diary with lead pencil attached, making the whole a convenient little pocket-book.

Aids to the Analysis of Foods and Drugs. By T. H. Pearmain and C. G. Moor, M.A., F.C.S. Second edition. London: Baillière, Tindall, and Cox. Pp. 206.

In this, the second edition, the authors have endeavoured to bring their handy little work as much up to date as possible; a considerable amount of the most recent information has been added, while many of the articles have been entirely re-written; the portion, however, dealing with drugs has been somewhat curtailed, as this subject is more thoroughly dealt with in their larger work on "The Analysis of Foods and Drugs."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 19, November 6, 1899.

Researches on Diamines. Diethylene Diamine (Piperazine.)—M. Berthelot.—Diethylene diamine is an interesting base both practically and theoretically. It is used in therapeutics under the name of spermine and piperazine. It was at first confused with the body of half its molecular weight, vinylamine and acetylamine. The author investigates this substance thermo-chemically, using for his experiments a product of which the analysis corresponds to the formula $C_4H_6N_2.6H_2O$. He first determines the heat of dissolution of the product of distillation, a determination which tends to establish the existence of a definite hydrate.

Some of the Characteristics of Diamines.—M. Berthelot.—This paper contains an account of the behaviour of diamine in presence of colouring matters.

Preparation and Estimation of Glycogene.—Armand Gautier.—The raw material from which the glycogene is to be extracted is roughly divided—when it is not a liquid—and thrown into one and a-half times its weight of boiling water. After filtration the pulp is again boiled with water, two or three litres of water being sufficient to extract 500 grms. of muscle. The tenth part of the liquor is titrated with neutral mercury acetate, to which a little acetate of potassium has been added. From this the amount of acetate solution required to precipitate the whole can be found. The filtrate contains the glycogene.

Rhamninose.—Charles and Georges Tanret.—Rhamninose is prepared by the hydrolysis of xanthorhamnine by very dilute sulphuric acid, by which process a mixture of rhamnose, galactose, and rhamninose is obtained. The pure rhamninose is then separated, and analysis and a study of its principal reactions assign to it the formula $C_{18}H_{32}O_{14}$. It is soluble in water and alcohol, but insoluble in acetone and acetic ether.

MEETINGS FOR THE WEEK.

Monday, 4th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "The Fire-proofing and Preserving of Timber," by Sherard Cowper-Coles, Assoc.M.I.C.E., &c.
—— Society of Arts, 8. (Cantor Lectures). "Enamelling upon Metals," by Henry Hardinge Cunynghame.
Wednesday, 6th.—Society of Arts, 8. "Artificial Silk," by Joseph Cash.
—— Society of Public Analysts, 8. "Note on Asafœtida," by C. G. Moor, M.A., F.I.C. "On some Analyses of Modern Dry Champagne," by P. Schridrowitz, Ph.D., and Otto Rosenheim, Ph.D. "On the Determination of the Iodine Value," by Dr. J. J. A. Wijs. "Treacle or Golden Syrup," by E. W. T. Jones, F.I.C. "On a Method for Distinguishing between Hops and Quassia," by A. C. Chapman, F.I.C.
Thursday, 7th.—Chemical, 8. Ballot for the Election of Fellows. "The Oxidation of certain Organic Acids in presence of Iron," by H. J. H. Fenton, M.A., and H. O. Jones, B.A., B.Sc. "Determination of the Constitution of Fatty Acids" (Part II.), by A. W. Crossley, M.Sc., Ph.D., and H. R. LeSueur, B.Sc. "On Sulphates of the Form $R'_2SO_4.2M''SO_4$, especially those of Isometric Crystallisation," by F. R. Mallet.
Friday, 8th.—Physical, 5. (At the City and Guilds Technical College, Finsbury). "Cylindrical Lenses," by Prof. Silvanus Thompson, F.R.S. "Exact Formulæ for Lenses," by T. H. Blakesley. "On an Organic Compound of great Double Refraction," by Prof. Silvanus Thompson, F.R.S.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2089.

RADIO-ACTIVITY DUE TO BECQUEREL RAYS.

By P. CURIE and Mdme. P. CURIE.

WHILST investigating the properties of the strongly radio-active materials, polonium and radium, we have found that the rays emitted by these substances, when in contact with inactive bodies, have the power of communicating their radio-activity, and that this induced radio-activity persists for a considerable time.

The radio-active material is powdered and placed on a horizontal plate; above this is placed, a few millimetres distant, the material to be tested supported on props. From time to time the upper plate is lifted, and taken immediately into the apparatus for electrical measurements, and its radio-activity determined by the conductivity which it communicates to air.

We have proved by this means the fact that the exposed plate has acquired a radio-activity, which increases with the time of exposure. At the end of some hours, however, this increase takes place very slowly, and the induced radio-activity seems to tend towards a limit. The induced radio-activity lasts for several days, but decreases, at first very rapidly, then less and less, and seems to be disappearing according to an asymptotic law.

In order to observe this phenomenon it is necessary to use substances strongly radio-active. Our experiments were performed with substances 5,000 to 50,000 times more active than uranium. The induced activity, observed immediately after exposure, varies between one and fifty times that of uranium, but was reduced to a tenth of its original value two or three hours later.

We have examined by this means the effect of Becquerel's rays on various substances—zinc, aluminium, brass, lead, platinum, bismuth, nickel, paper, barium carbonate, and bismuth sulphide. We were surprised not to find differences in the induced radio-activity in these different substances.

The aim of the present research was to find whether induced radio-activity is due to traces of the radio-active matter, which are carried in form of vapour or powder on to the exposed surface.

The analogous behaviour of the substances tried seems to point to this supposition. However, we believe that we have proved this theory to be incorrect, and that there does exist induced radio-activity. The gradual and regular disappearance of the induced activity, when the exposed plate is left in repose, seems to exclude the hypothesis of non-volatile powder, and it also would be difficult to conceive of the radiferous salts of barium being volatile. By washing the plates with water the radio-activity does not disappear, which would scarcely be the case were the activity due to a soluble powder.

Finally, we have devised with the greatest possible care an experiment which seems to us decisive. A very strongly radio-active substance (50,000 times more so than uranium) was enclosed in a metallic box, of which the bottom is formed of very thin aluminium. Plates in contact with the bottom of the box are rendered radio-active, the activity induced being ten to seventeen times greater than uranium. We obtain intense radio-active results by placing the substance to be impressed directly on the inducing substance. The phenomenon of induced radio-activity is a kind of secondary radiation due to Becquerel's rays, differing, however, from the phenomenon which is known to exist for Röntgen rays.

Indeed the secondary phenomena of Röntgen rays, as known at present, are given rise to at the moment when the body which emits them is struck by the Röntgen rays, and cease abruptly with the suppression of the latter.—*Comptes Rendus*, cxxix., No. 19, 1899.

THE SPECTRUM OF RADIUM.

By EUG. DEMARCAY.

I HAVE received during the present year several specimens of barium chloride from M. and Mdme. Curie containing radium in increasing proportion. Relatively to the increase of radiant power, the new lines show themselves more and more strongly, and further new lines have appeared, confirming the supposition that this spectrum is due to the radiant substance. In the first specimen I obtained, the radiant power was 7×10^4 times as great as that of uranium. The photographic spectrum contained lines comprised between $\lambda=5000$ and $\lambda=3500$. In this spectrum was noticed—

1. The spectrum of barium, very intense and complete.
2. That of the platinum electrodes and impurities—such as calcium, lead, &c.—being very weak, and reduced to their principal lines.

It contains a series of new lines, amongst which are several as strong as the strongest barium lines. These lines are as follows (the strongest intensity being marked 16, the weakest 1):—

λ.	Intensity.	λ.	Intensity.
4826·3	10	4533·5	9
4726·9	5	4458·0	3
4699·8	3	4436·1	8
4692·1	7	4364·2	3
4683·0	14	4340·6	12
4641·9	4	3814·7	16
4627·4	4	3649·6	12
4600·3	3		

$\lambda=4627{\cdot}4$ is the centre of a very characteristic symmetric nebulous band. The line marked λ 4558·0 is the same, only much weaker. All the lines are clear and sharp, and resemble those of barium in their appearance. It might be advisable to add to this list about ten other feebler lines; however, their faintness renders their origin uncertain. I believe it to be best to wait to publish these until radium has been obtained in a higher state of purity.

Finally, I may remark that, in the preceding list of the radium lines, those lines are missing which might be confounded with the eliminated lines of barium. I have also examined the less refrangible portion of this spectrum, and hope to be able to publish the results shortly.—*Comptes Rendus*, cxxix., No. 19.

THE DECOMPOSITION OF CARBONIC OXIDE IN THE PRESENCE OF METALLIC OXIDES.

By O. BOUDOUARD.

I HAVE already published the results I obtained in my research on the decomposition of carbonic oxide in the presence of metallic oxides at temperatures of 445° and 650° (*Bull. Soc. Chim.*, Series 3, vol. xxi., pp. 269 and 463). I have now continued these researches to 800°. I was, however, obliged to modify the apparatus used in the former experiments, and replace the glass tube by one of porcelain.

I used a porcelain tube glazed inside and out, 400 m.m. long, 30 m.m. outside diameter, and 24 m.m. inside diameter. This tube is connected with a capillary one,

also of porcelain, 200 m.m. long, 9 m.m. outside diameter, and 1 m.m. inside diameter. The end of this capillary tube is connected with a three-way tap, so that connection may be made with a mercury pump, or with the outside air.

The wide part of the tube is filled for a distance of about 100 m.m. with pumice containing cobalt, nickel, or iron oxides, which has already been submitted to the action of carbonic oxide at a temperature of 445°, and is covered with carbon resulting from the decomposition of the carbonic oxide. The remainder of the tube is filled with fragments of porcelain, and closed with a metal plug, cemented in, and fitted with a tap. It is from this side that the gas to be experimented on is admitted.

The apparatus thus fitted up is placed in a Mermet furnace in such a way that the part of the tube containing the pumice is directly exposed to the action of heat; the temperature is regulated by means of a Le Chatelier thermo-electric couple. The tube is filled with carbonic oxide, the two taps are closed, and the heat applied. After some time the gas is extracted by means of the pump, the apparatus being still hot; the capillary tube assists the immediate cooling of the gaseous mixture. The analysis made corresponds exactly with the condition of the mixture such as it really exists, for at the moment of extraction all contact between the gases and the carbon is instantly stopped.

The results obtained are as follows:—

Time. H. M.	Oxide of cobalt.		Oxide of nickel.		Oxide of iron.	
	CO_2.	CO.	CO_2.	CO.	CO_2.	CO.
0 8	4·4	95·6	3·0	97·0	3·2	96·8
0 30	5·5	94·5	4·8	95·2	—	—
0 45	5·6	94·4	—	—	—	—
2 15	7·0	93·0	6·3	93·7	—	—
4 0	6·5	93·5	6·7	93·3	—	—

The reaction of the decomposition of the carbonic oxide is thus affected by time. The quantity of carbonic acid formed increases in a regular manner, but as at 650° the decomposition of the carbonic oxide is limited. The experiments show that the reaction stops when the gaseous mixture contains 7 per cent of CO_2 and 93 per cent of CO.

It should further be noted that the speed of the reaction is much greater at 800° than at 650°; while at 650° it was necessary to heat for six hours to attain the limit, two hours sufficed at 800°.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 15.

ON THE EXPLOSIVE PROPERTIES OF CHLORATE OF POTASH.

By C. A. LOBRY DE BRUYN.

The recent terrible explosion of 156 tons of chlorate of potash has not yet been forgotten. In this case the chlorate was properly packed and stored, and there was no organic matter present.

Every explosive substance should properly explode exothermically, with disengagement of gas. Chlorate of potash fulfils this condition, since, according to Berthelot, the decomposition takes place according to the following formula:—

$$KClO_3 = KCl + O_3,$$

at the same time giving off 11,000 calories.

In 1891, during a research on *bellite* (4 parts of nitrate of ammonium to 1 part of dinitrobenzene) I showed that while bellite could be exploded by means of an ordinary detonator containing 1 grm. of fulminate of mercury, nitrate of ammonium requires, on the contrary, a much more powerful detonator. In this case there must be used at least 3 grms. of fulminate of mercury, or 10 to 30 grms. of bellite, itself acting as a fulminate.

The disaster at St. Helens appears to me to be analogous to a local fire which broke out in a gun-cotton magazine; the fire began slowly, the gun-cotton simply decomposed and burnt. After this the fire spread, and eventually a moment occurred when the gas generated could not escape sufficiently quickly; thus it collected and acted the part of a detonator and caused the remainder of the gun-cotton to explode with violence.

As a matter of fact chlorate of potash requires a much more powerful detonator than does gun-cotton; it is not combustible by itself, but it is probable that at St. Helens a portion of the salt was decomposed by a local fire in the immediate neighbourhood of the magazine, and that the rapid accumulation of gas caused the explosion above referred to.—*Zeitschr. f. Angewandte Chemie*, 1899, [27], p. 633.

A METHOD FOR THE DETERMINATION OF THE MELTING-POINT.

By M. KUHARA, Ph.D., and M. CHIKASHIGÉ, B.Sc.

Several different methods have hitherto been suggested for determining the melting-point of substances; one of which, that now in common use, consists in heating the substance to be experimented upon in a capillary tube, fastened to a thermometer, and immersed in a bath. It is usual, in this case, to take as its melting-point the temperature at which the substance begins to melt away from the walls of the capillary tube. This method, however, is very liable to give too high results, as it is a hard task to observe the exact point of fusion of that portion of the substance which is in contact with the walls of the tube, before the inner portion thereof reaches its melting-point: this is apparently higher than the real melting-point, owing to the bad conductivity of the air contained in the interstices of the substance and the consequent over-heating. We also find another disadvantage in this method, namely, that substances which cannot be pulverised—such as waxes, fats, &c.—are with difficulty introduced into the capillary tube.

We have recently devised a method which, we think, will eliminate all the disadvantages of the tube-method, and which, moreover, can easily be carried on in chemical laboratories.

In this new method, instead of a capillary tube, we make use of a pair of cover-glasses for microscopical purposes, cut in halves, between which the substance to be tested is introduced, either in powder, in crystals, or in thin slices. If the substance be in the state of powder, we can make the layer as thin as possible by pressing and sliding the two pieces with the fingers, so that the heat of the bath may at once be conducted throughout the whole mass. The surface exposed is very large compared with the quantity of the substance taken, and, consequently, its behaviour towards heat may be distinctly observed. Before the substance is melted the glass appears opaque, while it becomes transparent when fusion occurs. The thinner the layer the more distinct is the demarcation; but with volatile substances a quantity somewhat in excess of what is apparently essential should be taken, in order to make allowance for loss by volatilisation.

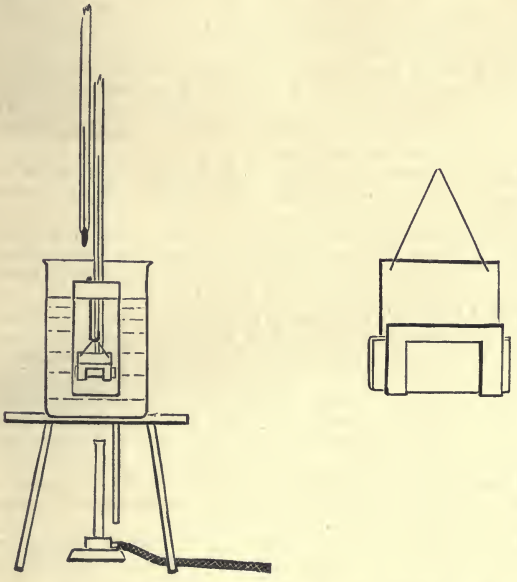
The pair of glass-pieces is then fastened to a holder made of platinum-foil, and tied, if necessary, with a piece of fine wire of the same material. The holder, which can easily be made by folding the foil and cutting it with scissors, as shown in the annexed figure, is suspended in a wide test-tube into which is inserted a thermometer close to the holder. The test-tube, serving as an air-bath, is immersed in the sulphuric acid bath almost to its mouth. The further steps of the process require no modification of the old methods.

The glass-pieces can be used any number of times, unless they are broken; this is considered another superiority over the tube-method.

The result of experiments with our method is given in the following table. The substances taken were purified by repeated crystallisation, and the temperatures given are the corrected ones :—

Substance.	I.	II.	III.	Mean.	M.-p. already known.	Observer.
	°	°	°	°		
Chloral hydrate	57·3	57·3	57·0	57·2	57	Meyer & Dulk.
Urea	132·1	132·1	132·3	132·2	132	Lubavin.
Phthalic acid..	203·2	202·7	203·0	203·0	203	Ador.
Phthalimide ..	233·6	233·7	233·6	233·6	233·5	Graebe.

The melting-point of phthalic acid has been a subject of discussion, the figures differing considerably in every case of determination. Lossen (*Annalen*, cxliv., 76) gives it as low as 184°, but Ador (*Annalen*, clxiii., 230) states that crystallised phthalic acid melts at 213°, and the powdered substance at 203°. Remsen (*Amer. Chem. Journ.*, viii., 30) ascribes the cause of such variation to the fact that phthalic anhydride, formed partly from the acid, lowers the melting-point of the mixture. In order to verify his view, small quantities of the acid, introduced into a U-tube, were heated over a paraffin bath at the temperatures of 140° and 170°, and the melting-point was found to be considerably lowered in both cases. This experiment was conducted by one of us a number of years ago, when working in his laboratory. We have found, however, with the new method, that both the crystallised and the powdered substances melt equally at the constant temperature of 203°, whether the air-tube be gradually heated or plunged at once into the bath at a temperature above 205°. This may probably be due to the fact that the anhydride formed is freely volatilised in our apparatus through the interstice of the two glass-pieces, and the remaining acid, kept pure, melts at its proper temperature. With our method we have never observed a temperature so high as 213° nor so low as 184°, while with the capillary-tube method we often noted a melting-point as low as 185°.



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A BIBLIOGRAPHY OF STEEL-WORKS ANALYSIS.

By HARRY BREARLEY.

(Concluded from p. 258).

MANGANESE: IV. Volumetric Estimation of Manganese (*continued*).

IV*c*. *Oxidation to Higher Oxides of Mn.*

IV.*c*. 1. *The Chlorate Process.*—

143. Hannay (*C. N.*, xxxvi., 212).—MnO_2 precipitated by heating with HNO_3 and $KClO_3$. In presence of Fe a double manganate of Fe and Mn is precipitated. Refers to the process as a means of separating Fe and Al.

144. Storer (*C. N.*, xxi., 195).—Oxidising value of HNO_3 and $KClO_3$ applied to assays of S and Cr compounds, &c.

145. Williams (*J. I. S. I.*, 1881, 656).—Filter MnO_2 from the strong acid solution. Titrate with oxalic acid and permanganate.

146. Meinecke (*J. C. S.*, lii., 531).—In the presence of Fe, warm dilute HNO_3 dissolves a little MnO_2 as precipitated by the $KClO_3$ process.

147. Julian (*C. N.*, lviii., 209; and *J. I. S. I.*, 1888, i., 376).—The precipitated solution is diluted, excess oxalic acid added, and titration with $KMnO_4$ speedily made. $KMnO_4$ standardised by adding oxalic acid to nitric solution from which MnO_2 has been filtered.

148. Stone (*J. I. S. I.*, 1883, 366).—The Mn precipitated with $KClO_3$ approximates to $10MnO_2.MnO$, and therefore oxidimetric estimations give low results. The standard solutions should be standardised with a spiegel of known composition. . . Separation with acetate and estimation as $Mn_2P_2O_7$ most accurate gravimetric process.

149. Raymond, Troilius, and Mackintosh (*J. I. S. I.*, 1883, 783).—MnO_2 dissolved in $FeSO_4$ and titrated. That the precipitate is not MnO_2 strongly repudiated; necessary to divide $KClO_3$ into small portions, and add alternately with strong HNO_3 in order to secure MnO_2. (See also Mackintosh, *C. N.*, xlviii., 176).

150. Stone (*C. N.*, xlviii., 273).—Defends his previous statement (see 148). The MnO_2 may be filtered from the hot as well as from the cold solution.

151. Mackintosh (*C. N.*, l., 75).—Influence of organic matter and iron on the process. Results a trifle low. Low results may sometimes be due to KCl in the $KClO_3$ giving rise to free HCl.

152. Troilius (*J. C. S.*, xlviii., 597).—The presence of $Fe(NO_3)_3$ facilitates precipitation with $KClO_3$. Lead, Cu, Ni, and Co are precipitated with the MnO_2, and give high results.

153. Raymond (*C. N.*, xlviii., 23).—After precipitating MnO_2, the solution is diluted with hot water before filtering.

154. J. T. (*C. N.*, lxxix., 157).—Cr steels are incompletely soluble in HNO_3, hence the chlorate process is open to error by the unattacked metal being soluble in the acid solution of $FeSO_4$ used in titrating.

155. Hampe (*J. I. S. I.*, 1885, 652).—Gives equations representing the changes. Neither HCl nor H_2SO_4 should be present, nor should large amounts of H_3PO_4 (see 158). The MnO_2 always contains foreign metals if such are in solution; Ni, Cu, Zn, and Sn are without influence; Co, Pb, and Bi cause high results; all such errors are eliminated by re-precipitating. $KClO_3$ should be added, little by little, so long as green vapours are evolved, boiled five or ten minutes, and filtered. Precipitate should be washed with water; HNO_3 unnecessary and may contain nitrous acid.

156. Cheever (*J. I. S. I.*, 1885, 736).—Strong HNO_3 is added finally, and boiled to completely decompose $KClO_3$. Precipitate must be washed with nitrous-free HNO_3; if washed with water Mn would be dissolved.

157. Reis (*J. C. S.*, lxii., 1132). — Modified process: use weaker acid and add $KClO_3$ all at once. Hampe (*ibid.*) strongly protests against these modifications.

158. Viard (*J. C. S.*, lxxii., ii., 519).—Process inapplicable in the presence of phosphoric acid, owing to the formation of trimanganic phosphate (see 132).

159. Gooch and Austin (*C. N.*, lxxvii., 269).—Short historical account of the process, possibility of $KClO_3$ being mechanically occluded in the MnO_2. Soda chlorate more soluble and more easily decomposed; precipitation complete if solution is just raised to boiling after final addition of $NaClO_3$; prolonged boiling leads to loss, probably due to solvent action of lower oxides of N in absence of Cl, dilution before filtration tends to dissolve Mn; oxidimetric estimation with arsenious acid and iodine; the precipitate not MnO_2, error may be 2 per cent or more if taken as such; solution of MnO_2, and precipitation at 80° C. with excess of permanganate in presence of $ZnSO_4$, throws down true MnO_2.

160. Reinhardt (*J. I. S. I.*, 1888, i., 377).—$KClO_3$ process not suitable for irons poor in Mn, and rich in Si. Describes a process similar to 171.

161. Norris (*C. N.*, lxiv., 242).—Process applied to slags by treating with HNO_3 and adding HF, boiling off excess HF and adding $KClO_3$. For ores, solution is effected with HNO_3, tartaric acid, and HF.

162. Ford and Bregowsky (*J. C. S.*, lxxiv., ii., 540).—SiO_2 is decomposed with a few drops of HF. The Mn, especially in ores, is more completely precipitated when HF has been used.

163. Jean (*J. C. S.*, lxiv., ii., 498).—Decomposes minerals with HCl, precipitates with soda carbonate, dissolves in HNO_3, and precipitates Mn with $KClO_3$.

IV. *c.* 2. *Other Oxidimetric Processes.*—

164. Parry (*C. N.*, xxix., 86). — Dissolve spiegel in HNO_3, evaporate, and heat to redness over Bunsen; cool, add sodium oxalate and HCl; heat, and collect CO_2 in graduated tube.

165. Galbraith (*C. N.*, xxxiii., 47).—Proceeds like Parry, but adds $FeSO_4$ and HCl and heats; the $FeSO_4$ unoxidised by the Cl is titrated (see 196).

166. Carnot (*C. N.*, lxviii., 51). — Evaporation of an HNO_3 solution to dryness, and ignition of the residue, yields an oxide remote from MnO_2. Repeated ignition below 200° C. improves matters, but the practice is uncertain.

167. Meinecke (*J. C. S.*, lii., 1139).—Precipitate Fe and Mn together with HgO and Br water. The MnO_2 is determined with oxalic acid and $KMnO_4$.

168. Reinhardt (*C. N.*, lviii., 173).—Mn precipitated with sodium acetate, Br, and ZnO; and MnO_2 titrated with oxalic acid and $KMnO_4$.

169. Low (*C. N.*, lxvii., 162).—Precipitation with ZnO and Br, and titration as above; ordinary constituents of ores do not interfere.

170. Vortmann (*C. N.*, lxii., 251).—Alum, iodine solution, and NaHO are used to precipitate MnO solution. Iodine determined in filtrate with thiosulphate. Alum ensures formation of MnO_2. Process available in presence of Fe and Al.

171. Reinhardt (*J. I. S. I.*, 1886, 393).—Fe precipitated with acetate and partly removed; Mn precipitated with Br and ammonia; MnO_2 titrated with $FeSO_4$, &c. This is spoken of as the Belani method. Meinecke's process of titrating is to add an excess of $KMnO_4 + ZnSO_4$, and determine excess $KMnO_4$ with antimony chloride. Muller (*J. I. S. I.*, 1886, 1022) recommends Meinecke's process, especially for highly manganiferous alloys.

172. Rosenthal (*C. N.*, xxxvi., 147). — Precipitates as $MnO_2.H_2O$ with H_2O_2 and ammonia. Large excess of H_2O_2 should beavoided; much $(NH_4)Cl$ is objectionable.

173. Barlow (*C. N.*, liii., 41).—Precipitates as above; precipitate completely insoluble in ammonia salts, and quite free from Ni, Co, or Zn. In presence of Fe the ignited $Fe_2O_3 + Mn_3O_4$ is distilled with HCl, the Cl being absorbed in KI, &c. (see 201).

174. Carnot (*C. N.*, lix., 16).—Precipitates entirely as MnO_2 with H_2O_2 and ammonia. Estimated with oxalic acid and permanganate.

175. McCulloch (*C. N.*, lix., 35).—Contends that Mn as precipitated by Carnot has varying composition, but approximately is Mn_7O_{13}. . . . Carnot later (*C. N.*, lix, 48) says the Mn is precipitated as $5MnO_2.MnO$ (Mn_6O_{11}).

176. Carnot (*J. I. S. I.*, 1893, ii., 531; 1895, i., 507). —Precipitate with H_2O_2, large amounts of NH_3 salts give low results. Zn, Cu, Ni, and Co form complex salts ($ZnO_5.MnO_2$), but are eliminated by re-precipitating. Fe causes no inconvenience if below 60 per cent; if more, preliminary separation with $KClO_3$. (*C. N.*, lxviii., 51).—Influence of HN_3 salts overcome by large amounts of H_2O_2. Mn may also be precipitated with Br and $(NH_4)HO$ in the cold as Mn_6O_{11}.

177. Ulzer and Bruhl (*J. I. S. I.*, 1896, ii., 442).—Precipitate with H_2O_2 and NaHO. Titrate with oxalic and $KMnO_4$.

178. Pattinson (*C. N.*, xxxix., 201).—Precipitated by hypochlorite or bromine and $CaCO_3$ in presence of $ZnCl_2$ or Fe_2Cl_6, dissolved in $FeSO_4$, and excess titrated with $K_2Cr_2O_7$ (see 213).

179. Lunge (*C. N.*, xli., 141).—That Ca salts have the same *rôle* as Zn salts in Pattinson's process. Processes for the analysis of Weldon mud discussed.

180. Weldon (*C. N.*, xli., 207).—Finds merely boiling slightly acidified $MnCl_2$ with enough bleaching-powder to produce a faint $KMnO_4$ colour to give results comparing with Pattinson's process, as 100 : 100·26.

181. Atkinson (*J. C. S.*, lii., 399).—Pattinson's process gives slightly low results, due to incomplete oxidation of the Mn.

182. Rossi (*J. I. S. I.*, 1891, i., 443).—Good account of Pattinson's process applied to manganiferous iron ores.

183. Mittenzwey (*C. N.*, ix., 253).—MnO solution made alkaline and shaken in a closed vessel. Amount of water needed to fill the partial vacuum equals amount of oxygen absorbed; calculation empirical; reaction certainly not so far as MnO_2 (see 76). Other bodies similarly estimated.

184. Schmid (*C. N.*, xiv., 107). — Freshly precipitated MnO_2 precipitates CuO_2 from $CuSO_4$. $CuO = MnO_2$ quantitatively true.

185. Carnot (*C. N.*, lxviii. 51).—Oxalic acid and $KMnO_4$ are the best reagents for oxidimetric estimations.

186. Kalman and Smolka (*C. N.*, li., 230; *J. I. S. I.*, 1885, 248).— Fuse with borax and alkaline carbonate, dissolve in $FeSO_4$, and titrate with permanganate. Suitable whenever the sample can be heated to Mn_3O_4.

187. Myhlertz (*J. C. S.*, lx., 366).—Fuse with sodium carbonate and KNO_3, digest with H_2O, reduce with alcohol; MnO_2 determined with $FeSO_4$ and $K_2Cr_2O_7$.

188. Alt (*J. C. S.*, lviii., 419).—By aspirating Br fumes through a previously boiled MnO solution containing $(NH_4)Cl$ and NH_3, MnO_2 is precipitated without staining the sides of the flask.

IV.*c.* 3. *Available Oxygen in Ores, &c.*—

189. Sherer and Rumpf (*C. N.*, xx., 302; and xxi., 48).—Comparison of Fresenius and Will's, iron, chloride of lime, and Bunsen methods.

190. Pattinson (*C. N.*, xxi., 267).—The high percentage of available oxygen given by Fresenius and Will's process is not generally due to FeO. Describes a modified iron method.

191. Paul (*C. N.*, xxi., 16).—Dissolve ore along with oxalic acid in H_2SO_4; titrated with permanganate.

192. Harvey (*C. N.*, xlvii., 2).—Heats with $SnCl_2$ and HCl, and estimates excess $SnCl_2$ with Fe_2Cl_6 and $K_2Cr_2O_7$.

193. Charpentier (*C. N.*, lii., 86).—Pass liberated Cl into $FeSO_4$; KCNS and standard KHO added until solution is decolourised. Or Cl collected in $AgNO_3$, add drop $Fe(NO_3)_3$, and titrate with KCNS. The reaction sensitive to 1/3,000,000.

194. Lunge (*J. C. S.*, lviii., 1470).—Ore decomposed according to the equation—

$$MnO_2+H_2O_2+H_2SO_4=MnSO_4+2H_2O+O_2;$$

the O is measured in the nitrometer.

195. Carnot (*C. N.*, lxviii., 15 and 301).—The oxide reacts with a nitric solution of H_2O_2, and the evolved O is measured. Jones (*C. N.*, lxviii., 305) draws attention to previous proposals, and also to the fact that higher oxides of Pb may be similarly estimated.

IV.*d. Indirect Processes of Estimating Manganese.*—

196. Riley (*C. N.*, xxxv., 175). — Dissolve in dilute H_2SO_4; allow 5 per cent for C, &c.; difference, Mn. Results low, owing to soluble organic matter; obviated by taking nitric acid solution to dryness, dissolving in HCl, and reducing with Na_2SO_3. Methods of Parry and Galbraith (164 and 165) are undesirable ones.

197. Holdich (*C. N.*, xlix., 9).—As Riley; but recommends a subtraction of determined Si.

198. Atkinson (*C. N.*, xlix., 25).—Subtracts Fe and Si + 6 per cent for ferro-manganese. Results not so regular as with spiegels.

199. Parry (*C. N.*, lxvii., 296).—Allows 6 per cent for spiegel and 7 per cent for ferro-manganese.

200. Troilius (*J. I. S. I.*, 1883, 784). — 7·5 per cent allowed for impurities if Fe is less than 20 per cent; 6·5 if Fe is 20 to 45 per cent; 6·0 per cent if Fe is 45 to 65 per cent; and 5·5 per cent for upwards of 65 per cent Fe. These are Ledebur's figures.

201. Diehl (*J. C. S.*, l., 101).—Mn and Fe are precipitated with Br and NH_3; ignited; Fe determined volumetrically, Mn by difference.

IV.*e. Miscellaneous Volumetric Processes.*—

202. Leison (*C. N.*, xxii., 210).—Mn completely precipitated as oxalate; estimated by titration with permanganate. The separation of metals as oxalates is discussed by Luckow (*C. N.*, lv., 73).

203. Blum (*J. C. S.*, lx., 1293).—Boiling ammoniacal solution containing Mn, Fe, $(NH_4)Cl$, and tartaric acid is titrated with ferrocyanide; acetic acid used as indicator.

204. Fresenius ("Quant. Anal.").—Adds an excess of ferricyanide, and determines the ferrocyanide formed by means of $KMnO_4$.

205. Nass (*J. C. S.*, lxvi., 1482).—Classen's process (precipitation as oxalate) useless for estimating Mn, Co, or Ni.

206. Neumann (*C. N.*, lxxii., 212).—Neutral solution precipitated with alkaline sulphide; excess of sulphide estimated. Process applied to a dozen other metals.

207. Rössler (*C. N.*, xl., 169).—MnO solution, free from halogens and organic matter, mixed with standard Ag solution; Ag precipitated with sodium carbonate; excess $(NH_4)HO$ added; filtrate titrated with KCNS. A similar process for cobalt (*C. N.*, xli., 184).

208. Purgotti (*J. C. S.*, lxxii., ii., 349).—MnO_2 reacts with hydrazine sulphate to form N, which is measured at N. T. P. Per cent Mn calculated from this.

V. Detection of Manganese.

209. Böttger (*C. N.*, xxiv., 192).—Fragment of the substance dropped into fused $KClO_3$. Peach-blossom red indicates Mn.

210. Hillebrand (*C. N.*, lxxviii., 80).—During fusion an oxidising atmosphere must be in the crucible, otherwise negative results are obtainable when Mn is present.

VI. Miscellaneous Notes.

211. Kern (*C. N.*, xxxviii., 268).—Mn unequally distributed in alloys. A difference of 2·2 per cent observed.

212. Carnot and Goutal (*J. C. S.*, lxxii., ii., 555).—If in small quantity, Mn is present in iron as silicide or sulphide. In larger amounts, it is either partly dissolved or in combination with the iron.

213. Ledebur (*J. I. S. I.*, 1884, 269).—Compares Volhard, chlorate, and Pattinson processes. In $KClO_3$ process the precipitated solution was heated near boiling-point for two hours; results 0·5 to 1·0 per cent too low; very difficult to wash free from $KClO_3$. Pattinson's process most meritorious, but Cu, Co, and Ni cause plus errors.

214. Saniter (*J. I. S. I.*, 1894, 613).—Reviews Pattinson, Volhard, pyrophosphate, and Mn_3O_4 methods. The latter trustworthy if Mn has been precipitated as hydrated dioxide.

215. Rurup (*J. I. S I.*, 1896, i., 534).—Examines estimation as sulphide, Mn_3O_4; chlorate process (Ford's), weighing as Mn_3O_4; Volhard's, separation of Fe with Na_2SO_4 and titrating with $KMnO_4$; and the $KClO_3$ volumetric process. All accurate for steel works purposes.

216. Juptner (*J. I. S. I.*, 1895, i., 507).—Draws attention to various atomic weight values as a cause of differences.

217. Hogg (*C. N.*, lxviii., 163).—Cyano-nitride of titanium occurs in all high-grade spiegels and ferro-manganeses. In the latter, half a million separate crystals are calculated to occur in each cubic inch; they are separated by elutriating the nitric acid residue.

Spectroscopy and Spectrum Photography.—At the University College, London, a Course of Eight Lectures dealing with the methods of Spectroscopy especially in connexion with the Photography of the Spectrum will be given by Mr. E. C. C. Baly, on Friday Evenings, at 5.30 o'clock, commencing on January 19th, 1900. Fee for the course, One guinea. The following subjects will be treated and illustrated by experiments:—

The simple theory of refraction and diffraction.

The history of the determination of the modern standards of wave-lengths.

The Prism Spectroscope and its integral parts.

The comparison of spectra and determination of wave-lengths visually and photographically with Prism apparatus.

The Grating Spectroscope. Rowland's concave gratings; their mounting and adjustment.

The determination of wave-lengths with the grating.

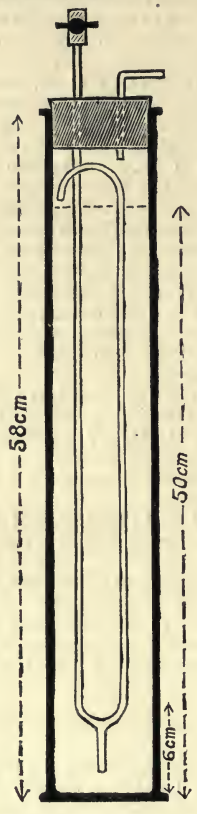
Photography of the Spectrum.

Methods of producing emission and absorption spectra, Fluorescence and Phosphorescence.

A DISSOLVER.

By ARTHUR JOHN HOPKINS.

AN apparatus for hastening the solution of salts has been described by Richards (*American Chemical Journal*, xx., 189). That such devices will supplant the good old methods of heating or stirring is not to be supposed; but heating is often proscribed by the nature of the salt or the requirement of a constant temperature, and stirring by hand is laborious and inconstant: and although both constant temperature and constant circulation are supplied by mechanical stirrers, yet it is possible that the necessity for mechanical devices has deterred many a chemist from entering upon the study of solubilities. A field may therefore be open for an apparatus serving the same purpose as a stirrer and constructed from material with which the chemist is already familiar.



Richards's dissolver, although of simple construction, is very efficient, and moreover is automatic, in that it requires no stirrer. Its efficiency is obviously limited to such salts as can form saturated solutions of much greater specific gravity than the solvent, and further limited to the formation of non-saturated solutions of these salts. The rate of flow in a purely automatic dissolver will rapidly approach zero, as the specific gravity of the solvent gains on that of the saturated solution. In fact, at any one moment the rapidity of solution varies as the square of the velocity of the solvent passing the crystals.

In the hope of making a dissolver which shall be universally applicable without resorting to mechanical stirrers, an attempt has been made in this laboratory to apply a well-known device to this problem. The result is a dissolver of simple construction and great efficiency, which will rapidly prepare solutions of any specific gravity.

The accompanying illustration shows such an apparatus. An ordinary glass cylinder of any convenient size may be used. The one represented holds 2200 c.c.* Through one hole of a two-holed stopper is passed a straight glass tube of about 6 m.m. bore, fitted at the upper end with a short rubber tube and screw-cock. The lower end of this glass tube is fused, or bound by aid of rubber connection tubing, to one arm of a Y-tube, the lower arm of which reaches nearly to the bottom of the cylinder. The third arm of the Y-tube meets a second glass tube, which reaches up nearly to the stopper, and there curves down to give direction to the concentrating solution. The second hole of the stopper carries a short exit tube bent at a right angle, the lower portion of which extends to a point just below the bottom of the stopper.

To use the dissolver, introduce the desired quantity of water or other solvent with the weighed quantity of salt to be dissolved, then put the stopper, carrying its tubes, firmly into position, and apply, by means of a filter-pump attached to the short right-angled tube, enough suction to overcome the water pressure of 44 c.m. A current of air, regulated by the screw-cock to prevent vibrations in the Y-tube, follows the water down the long tube in continuous column, but continues only as far as the junction of the Y-tube, for there it is broken into little columns alternating with columns of the saturating solution drawn up through the lower arm of the Y-tube. These broken columns of air, rising through the curved tube, lift the solution drawn directly from the crystals, and throw it out upon the least saturated solvent at the top. The air escapes through the short tube, and the fresh solvent, which occupied the upper position in the cylinder at the beginning, sinks down to dissolve more of the crystals below. When a carefully regulated and not too great suction is applied, there is a continuous and rapid current of the solution passing the crystals, while the saturated solution may be seen streaming from the crystals to the lower end of the Y-tube.

To test the efficiency of this apparatus, 30 grms. of copper sulphate, in crystals of about 2 grms. each, were dissolved in 200 c.c. of distilled water at 19°. For this purpose a cylinder of about one-tenth the size described was selected. Complete solution took place in about forty minutes.

In order to prepare a solution of ammonium carbonate for use in qualitative analysis, a very large stand-cylinder which had formerly served as a generator of hydrogen sulphide, was employed. The proper tubes were attached to the stopper, and, when 1 kilo. of commercial ammonium carbonate, 1 litre of concentrated ammonium hydroxide, and 4 litres of distilled water had been placed in the stand-glass, suction was applied, and in thirty minutes all but about 20 grms. of the salt had been dissolved. Dissolving this salt in such large quantities by the usual method takes not less than four or five consecutive hours, and in busy laboratories a day or two of intermittent stirring is often allowed. Assembling the parts of the apparatus and affecting the solution, in the case cited, required less than forty-five minutes.

This dissolver has been used, in a bath of constant temperature, for making saturated solutions of copper sulphate, and for determining the solubility of this salt at different temperatures. For this purpose the lower end of the short reduction-tube was protected, and the entering air was washed through caustic potash and then through sulphuric acid, and again washed on leaving through weighed sulphuric acid tubes. Completely saturated solutions were obtained in about ninety minutes. This work will be taken up again in this laboratory and reported upon.

The dissolver here described, like that of Richards, requires no attention, and is very easily constructed in a few minutes from ordinary laboratory material. It in-

* It is best to choose a cylinder of such size that the quantity of solution desired shall fill it to a point just below the curved tube.

volves no mechanical difficulties, is universally applicable, and seems as rapid as any of the mechanical stirrers or shakers.—*American Chemical Journal*, November, 1899, p. 407.

A NEW VOLUMETRIC METHOD FOR MAGNESIUM.*

By RICHARD K. MEADE.

One of the elements for which, so far, no satisfactory volumetric method of determination, of general application, has been found, is magnesium. Stolba (*Chem. Centrbl.*, 1866, 728) suggested a volumetric method depending upon the fact that 1 molecule of magnesium ammonium phosphate required 2 molecules of mineral acid for solution. Hart and Sutton both describe the method in detail, in their works upon volumetric analysis, and call attention to its accuracy. Hartzell, a student in the laboratory of Lafayette College, in his thesis work for graduation, in 1897, made use of the method in determining magnesia in cement, and the result of his investigations also showed the method to be fairly accurate. The great objection to Stolba's method, particularly if it is resorted to as a time-saver, is the tedious washing of the precipitated magnesia with alcohol, in order to get rid of the ammonia, making the volumetric determination very little, if any, quicker than the gravimetric. In any event, so far as I know, the method is very little if ever used, even in commercial laboratories where magnesia determinations are a part of the daily routine.

Analogous to the phosphates are the arsenates. If instead of adding sodium phosphate to an ammoniacal solution containing magnesium we add sodium arsenate, magnesium ammonium arsenate, corresponding to magnesium ammonium phosphate, is precipitated. This reaction is of course a familiar one, since it is the one upon which the usual gravimetric determination of arsenic is based. Now if the magnesium in a solution can be entirely precipitated as a double arsenate of magnesium and ammonium, if the magnesium and arsenic in this compound bear a fixed ratio to each other, if the precipitate can be collected and washed free from sodium arsenate, then clearly any volumetric method which will give us the weight of arsenic in the precipitate will also tell us indirectly the amount of magnesium in the solution. From the formula of the double salt, $Mg_2(NH_4)_2As_2O_8+H_2O$, it will be seen that one atom of magnesium is equivalent to one atom of arsenic, and consequently the ratio between the magnesium and arsenic is 24·28 : 75·01.

As the first step looking to the formulation of a volumetric method along these lines, a stock solution of magnesium was prepared as follows:—Fifty grms. of pure magnesium chloride were dissolved in about 700 c.c. of water, and a little ammonium oxalate added to precipitate any traces of calcium present. The solution was allowed to stand for a day, when the very slight precipitate of calcium oxalate was filtered off. A sufficient quantity of ammonium oxalate to convert all the magnesium in the solution to magnesium oxalate was next added, and the solution evaporated to small bulk over a water-bath. The separated magnesium oxalate was collected, washed, dried, and ignited, first at a low temperature, and then at a higher, until finally at a red heat. Of the pure magnesium thus obtained, 5 grms. were dissolved in dilute hydrochloric acid and the solution diluted to 2 litres. Each 50 c.c. of this solution should have been equivalent to 0·2500 grm. of magnesium oxide. Checked by precipitation with sodium phosphate, 50 c.c. gave—

I. 0·6900 grm. of $Mg_2P_2O_7$, equivalent to 0·2497 grm. of MgO.

II. 0·6891 grm. of $Mg_2P_2O_7$, equivalent to 0·2493 grm. of MgO.

Checked by evaporation to dryness and ignition of the residue, 50 c.c. gave—

0·2490 grm. of MgO.
0·2498 grm. of MgO.

The average of the four determinations is 0·2495 grm. of MgO.

A search into the literature on the solubility of the magnesium ammonium arsenate showed the precipitate to be less soluble where an excess of sodium arsenate was present in the ammoniacal solution; accordingly, wherever the magnesium was precipitated by sodium arsenate, a considerable excess of the precipitant was used. The precipitate of course must be washed with dilute ammonia water, and, as it is not entirely insoluble in this medium, the volume of the washing fluid should be kept as small as possible.

Following these points, 50 c.c. of the stock solution were diluted to 500 c.c., and 50 c.c. of sodium arsenate (10 per cent) solution added; then ammonia, drop by drop, with constant stirring until the precipitate began to form. At this point the addition of ammonia was interrupted and the solution stirred for five minutes, after which one-sixth the volume of the solution of strong ammonia was added and the mixture stirred for five minutes longer and allowed to stand over night. In the morning the precipitated magnesium ammonium arsenate was collected in a Gooch crucible, dried, and ignited at a very low temperature, and weighed as magnesium pyroarsenate, containing 25·94 per cent of magnesium oxide. The results were:—

No.	$Mg_2As_2O_7$. Grm.	Equivalent to MgO. Grm.
1	0·9599	0·2490
2	0·9545	0·2476
3	0·9592	0·2488
4	0·9573	0·2483
Average		0·2484
Instead of		0·2495
Difference		0·0009

As a further test the magnesia from 50 c.c. of the stock solution was precipitated as described, dissolved in dilute hydrochloric acid, and the arsenic thrown out of solution with hydrogen sulphide. The magnesium remaining was then determined as pyrophosphate with the following results:—

No.	$Mg_2P_2O_7$. Grm.	Equivalent to MgO. Grm.
1	0·6883	0·2490
2	0·6865	0·2484
3	0·6870	0·2486
Average		0·2487
Instead of		0·2495
Difference		0·0008

In the same manner, the magnesium in 50 c.c. of the stock solution was precipitated as magnesium ammonium arsenate, dissolved in hydrochloric acid, and the arsenic determined as magnesium pyroarsenate by addition of magnesia mixture. The results were:—

No.	$Mg_2As_2O_7$. Grm.	Equivalent to MgO. Grm.
1	0·9590	0·2488
2	0·9536	0·2474
3	0·9552	0·2478
Average		0·2481
Instead of		0·2495
Difference		0·0014

* Read before the Lehigh Valley Section of the American Chemical Society, May 16, 1899. From the *Journal of the American Chemical Society*, vol. xxi., No. 9, September, 1899.

These three sets of results, while a little low, showing that a slight loss of magnesia is incurred, probably due to solution of the precipitate in the mother-liquor and the wash-water, nevertheless fall well within the limits of allowable variation for technical work, and show the ratio between the magnesium and arsenic to be constant.

The next step was to find a suitable volumetric method for determining the arsenic. This being in the state of arsenic acid excluded all methods supposing the element to be in the condition of lower oxidation. The methods of Pierce and McCay depending upon the precipitation of the arsenic as silver arsenate by an excess of standard silver nitrate and the determination of either the silver in the precipitate or the excess of silver in the solution by titration with sodium thiocyanate, were also not considered, as both time and expense made them unsuitable for commercial work.

Of the methods depending upon the reduction of the arsenic to arsenious acid and the titration of the latter by standard iodine, that making use of the reaction between arsenic acid and potassium iodide in acid solutions, offered the best field for investigation, and, following the method as laid down by Gooch and Browning (*Am. J. Sci.*, [3], xl., 66), several determinations were made. The process followed consisted in dissolving the precipitated arsenate in dilute sulphuric acid, adding an excess of potassium iodide and 10 c.c. of sulphuric acid (1 : 1), and diluting to 100 c.c. The solution was boiled rapidly until the volume reached 40 c.c. and the free iodine in the solution destroyed by careful addition of sulphurous acid (roughly made about one-half normal). Sodium carbonate was then added until the solution was nearly neutral, and next an excess of sodium bicarbonate over what was required to make it so. The arsenious acid was then titrated with standard iodine solution. This latter was made by dissolving 52·24 grms. of pure re-sublimed iodine in a solution of 75 grms. of potassium iodide in 200 c.c. of water and diluting to 1 litre. Each c.c. of this solution should be equivalent to 0·005 grm. of magnesium oxide. The following satisfactory results were obtained by this method :—

No.	Stock solution taken.	Equivalent to MgO.	Iodine required.	Equivalent to MgO.
	C.c.	Grm.	C.c.	Grm.
1	50	0·2495	49·6	0·2480
2	50	0·2495	49·7	0·2485
3	25	0·1247	24·9	0·1245
4	25	0·1247	24·9	0·1245
5	10	0·0499	9·9	0·0495
6	10	0·0499	10·0	0·0500

The time required to determine the arsenic by this method was from one-half to three-quarters of an hour.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 16th, 1899.

Professor THORPE, F.R.S., President, in the Chair.

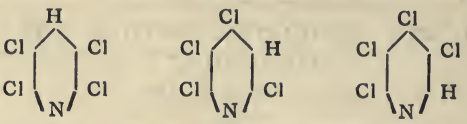
CERTIFICATES were read for the first time in favour of Messrs. Herbert William Hart, 13, Lynwood Villas, Darwen, Lancashire; Henry William Hutchin, Basset Road, Camborne.

The following Certificate was authorised by Council :—Frank J. Pye, Towrang, New South Wales, Australia.

Of the following papers, those marked * were read :—

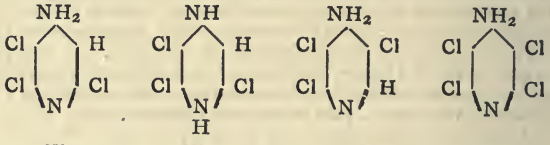
*143. "*The Chlorine Derivatives of Pyridine.* Part IV. *The Constitution of the Tetrachloropyridines.*" By W. J. SELL, M.A., F.I.C., and F. W. DOOTSON, M.A.

The three theoretically possible tetrachloropyridines have all been obtained (*Trans.*, 1898, lxxiii., 432), and are represented by the formulæ I., II., and III. respectively :—



I. II. III.

Having already proved (*Trans.*, 1897, lxxi., 1081) that the compound melting at 90—91° has the constitution represented by Formula I., the authors show in the present paper that the isomer which melts at 21—22° is represented by Formula III., and hence Formula II. must represent the constitution of the third isomer, which melts at 74—75°. Treatment with ammonia converts the compound melting at 21—22° into an aminotrichloropyridine, which is quite different from that described by Stokes and Pechmann (*Amer. Chem. Journ.*, 1886, vi., 377), and shown by them to have either the Formula IV. or possibly IV.A ; as the new compound contains an amino-group in the γ-position, it must be represented by Formula V.



IV. IV.A. V. VI.

That the γ-position is occupied by the amino-group is evident from the fact that when this new compound is heated with phosphorus pentachloride, the aminotetrachloropyridine obtained is that which has been shown by Stokes and Pechmann, and by the authors, to have the constitution represented by Formula VI.

*144. "*Contributions to our Knowledge of the Aconite Alkaloids.* Part XV. *On Japaconitine and the Alkaloids of Japanese Aconite.*" By WYNDHAM R. DUNSTAN, F.R.S., and HAROLD M. READ.

The authors have investigated the properties of the alkaloids of Japanese aconite, *A. Fischeri* ("kuza uzu"), including those of japaconitine, the crystalline toxic alkaloid examined by Wright and Luff in 1879, who assigned to it the formula $C_{66}H_{88}N_2O_{21}$. Later workers, Mandelin, Lübbe, and, more recently, Freund and Beck, have asserted that japaconitine is identical with aconitine, the crystalline toxic alkaloid of *Aconitum napellus*.

The results obtained in the present investigation do not confirm these statements, but lead to the conclusion that japaconitine is a distinct alkaloid, the composition and properties of which, however, do not agree with those ascribed to it by Wright and Luff.

Japaconitine crystallises in colourless needles which melt at 204·5° (corr.). The crystallographic characters differ from those of aconitine. The base is soluble in acetone, alcohol, chloroform, and in ether, but almost insoluble in water and light petroleum. Its physiological action closely resembles that of aconitine. It contains four methoxyl groups, one acetyl group, and one benzoyl group. Its composition is provisionally represented by the formula $C_{21}H_{29}(OCH_3)_4(CH_3CO)(C_6H_5CO)NO_3$, which seems to agree best with the analytical data for the base and its derivatives. Japaconitine furnishes a series of well crystallised salts, of which the *hydrochloride* (m. p. 149—150°), the *hydrobromide* (m. p. 172—173°), the *hydriodide* (m. p. 207—208°), the *aurichloride* (m. p. 231°), and the *nitrate* (m. p. 194°) are described. Like aconitine, japaconitine is dextrorotatory, the salts being lævorotatory. The specific rotation of japaconitine is, however, much greater than that of aconitine.

When partially hydrolysed by dilute acids, japaconitine furnishes acetic acid, and a new crystalline base,

japbenzaconine, in accordance with the equation $C_{34}H_{49}NO_{11}+H_2O=C_{32}H_{47}NO_{10}+C_2H_4O_2$. It crystallises in rectangular plates which melt at 182—183°. Its lævorotation is nearly twice that of benzaconine. The salts crystallise with extreme readiness. The *hydrochloride* (m. p. 253°), the *hydrobromide* (m. p. 205°), the *aurichloride* (m. p. 228°), and the colourless *aurichlor*-derivative (m. p. 178°) are described.

Japbenzaconine is hydrolysed on treatment with acids or alkalis, yielding benzoic acid and a base, *japaconine*, in accordance with the equation $C_{32}H_{47}NO_{10}+H_2O=C_{25}H_{43}NO_9+C_7H_6O_2$. Japaconine has been obtained only in an amorphous condition, even the salts crystallise with great difficulty. The *hydrobromide* melts at 221°.

When japaconitine melts, it gradually suffers decomposition into acetic acid and a new crystalline base, *pyrojapaconitine*, $C_{32}H_{45}NO_9$. The crystalline *hydrochloride* (m. p. 175—176°), *hydrobromide* (m. p. 208°, or in another form at 241°), and *aurichloride* (m. p. 161°) are described. Both pyrojapaconitine and its salts are strongly lævorotatory.

Pyrojapaconitine is readily hydrolysed by alkalis or acids, yielding *benzoic acid* and *pyrojapaconine*, $C_{25}H_{41}NO_8$. Neither the base nor its salts have been crystallised.

Japaconitine yields a *triacetyl*-derivative; and also a *monomethyl*-derivative by decomposition of the *methiodide* with potash.

It is evident that the properties of japaconitine and its derivatives are distinct from those of aconitine and its derivatives, although there is a strong general resemblance between the two groups.

Besides the crystalline japaconitine, Japanese aconite roots were found to contain a small proportion of its first hydrolytic product, japbenzaconine.

Discussion.

Professor Tilden inquired how many aconitines were known possessing the physiological action of the original alkaloid from *Aconitum napellus*, and pointed out the remarkable change in properties resulting from the elimination of the acetyl group from aconitine.

Mr. D. Howard said that it would be of extreme interest if any light could be thrown upon the relation of the chemical constitution of the aconite alkaloids to their physiological action, the problem being of the highest importance.

Professor Dunstan, in reply, stated that aconitine from *A. napellus*, pseudaconitine from *A. ferox*, and japaconitine from Japanese aconite (probably *A. Fischeri*) exerted very similar physiological action. The relationship between the chemical constitution and the physiological action of these alkaloids and their derivatives was being investigated by Professor Cash and himself. They had already published (*Phil Trans.*, 1898, cxc., B, 239) an account of the work as far as it related to aconitine, benzaconine, and aconine, and had paid special attention to the almost entire loss of toxic power which results from the elimination of the acetyl group from aconitine. In fact benzaconine and aconine, especially the latter, were found to be, in certain respects, physiologically antagonistic to aconitine.

*145. "*The Dissociation Constants of very Weak Acids.*" By James Walker and William Cormack.

A form of apparatus is described which enabled the authors to measure the electric conductivity of very weak acids with considerable accuracy, the method of experiment adopted being especially applicable to such acids as are gaseous under ordinary conditions.

The following table contains the chief results obtained, hydrochloric and acetic acids being added for purposes of comparison. The first column of figures gives the dissociation constants calculated by Ostwald's formula, the second column gives the percentage degrees of dissociation in decinormal solution, these numbers being proportional to the avidities of the acids:—

	$k \times 10^{10}$.	100 m.
Hydrochloric acid	—	91·4
Acetic acid	180,000	1·30
Carbonic acid	3,040	0·174
Hydrogen sulphide	570	0·075
Boric acid	17	0·013
Hydrocyanic acid	13	0·011
Phenol	1·3	0·0037

These results are in general harmony with the hydrolytic experiments of Shields.

Discussion.

Mr. L. M. Jones asked whether the weak inorganic acids examined obeyed Ostwald's dilution law, as considerable differences occur with strong inorganic acids, and whether the dissociation in all cases nroceeded with the formation of only the monovalent anion.

Mr. Vernon Harcourt hoped that the actual measurements of the conductivity were given in the paper, and not only the inferences from these measurements. Careful physical measurements, where all conditions were recorded, had a value more certain to endure than the theory used to interpret them.

Professor Tilden mentioned that, at his suggestion, one of his students had lately studied the conductivity and hydrolytic effects of azoimide in the expectation of finding it a tolerably strong acid. The results of these experiments, which would shortly be communicated to the Society, however, led to the conclusion that azoimide is a weak acid standing very near to hydrocyanic acid.

Professor Walker, in reply, said that all the acids investigated obeyed Ostwald's dilution law, and that the primary dissociation in each case was therefore into one atom of hydrogen and the rest of the molecule.

Whether the theory of electrolytic dissociation were finally accepted or rejected in its present form, the "degree of dissociation" would always remain a valuable and, indeed, indispensable magnitude where aqueous solutions of electrolytes were concerned, for by its means alone is it possible to calculate chemical equilibrium in such solutions. The interpretation and the name of the magnitude might be changed, but the magnitude itself is a fundamental one.

*146. "*Preparation and Properties of Solid Ammonium Cyanate.*" By James Walker and John K. Wood.

In a preliminary communication (*Proc.*, 1898, 108), the authors showed that pure solid ammonium cyanate might be prepared by mixing cooled ethereal solutions of ammonia and cyanic acid. The same substance can be produced by mixing ammonia gas and cyanic acid vapour at the ordinary temperature, provided the reacting gases are sufficiently diluted with some indifferent gas.

Measurements of the rate of transformation of the solid cyanate into urea showed that the rapidity of transformation increases very rapidly with rise of temperature, and that the presence of moisture greatly accelerates the action. About 3 per cent of the cyanate is decomposed, with formation of ammonia.

The molecular heat of transformation of solid cyanate into solid urea is 49K; the molecular heat of formation of solid cyanate is 738K; and the molecular heat of solution in water is −62·3K. From these numbers, it appears that the molecular heat of transformation in aqueous solution is 75K.

Ethylammonium cyanate is rapidly transformed into ethyl-urea at the ordinary temperature. When ethereal solutions of aniline and cyanic acid are mixed, the substance which separates is not phenyl-ammonium cyanate, but phenyl-urea.

*147. "*Etherification of Derivatives of β-Naphthol.*" By William A. Davis.

The author has studied quantitatively the etherification of a considerable number of substitution derivatives of β-naphthol by means of alcohol and sulphuric acid. It is shown that a single group occupying position 1 has a most

remarkable effect in limiting etherification, although the same group in position 3' exercises little influence.

The inhibiting influence of ortho-groups on the etherification of phenols, and of substituted benzoic acids, as studied by Victor Meyer and others, is fully discussed; the conclusion arrived at is that the stereochemical hypothesis proposed by V. Meyer to explain his results is not justified by facts.

The following ethers are described:—3'-*bromo*-β-*methoxynaphthalene*, m. p. 105°; 1-*bromo*-β-*methoxynaphthalene*, m. p. 82—83°; 1-*chloro*-β-*methoxynaphthalene*, m. p 68°; 1 : 3'-*dibromo*-β-*methoxynaphthalene*, m. p. 100°; 3'-*bromo*-β *ethoxynaphthalene*, m. p. 80°; 1-*bromo*-β-*ethoxynaphthalene*, m. p. 66°; 1-*chloro*-β-*ethoxynaphthalene*, m. p. 58°; 1 : 3'-*dibromo*-β-*ethoxynaphthalene*, m. p. 94°; 1 : 3'-*chlorobromo*-β-*ethoxynaphthalene*, m. p. 77°; 3'-*bromo*-β-*propoxynaphthalene*, m. p. 63·5; 1-*bromo*-β-*propoxynaphthalene*, m. p. 35—36°; 1 : 3'-*dibromo*-β-*propoxynaph:halene*, m. p. 75°; and 1 : 3'-*chlorobromo*-β *propoxynaphthalene*, m. p. 60·5°.

148. "*On the Determination of Transition Temperatures.*" By H. M. Dawson, Ph.D., B.Sc., and P. Williams, B.Sc.

While the influence of temperature on homogeneous and heterogeneous equilibrium is a continuous one, the so-called "condensed systems" are characterised by the existence of a transition temperature. At this temperature, the system suddenly undergoes a complete change. The second form of the system, which is stable at the higher temperature, is entirely re-transformed into the first on lowering the temperature below that of the transition-point.

Various methods have been employed for the determination of such transition temperatures; for example, the dilatometric, the thermometric, and the various identity methods. The latter depend upon the fact that the saturated solutions of the systems which are capable of mutual transformation become identical at the transition-temperature. In consequence of this, the properties of the saturated solutions corresponding to the various solubility curves emanating from the transition-point assume the same value at this temperature. In choosing a suitable property of the saturated solution for investigation, attention must be paid to the three following points:—(1) The property in question must be measurable accurately and rapidly; (2) it must show a notable variation for small changes in the composition of the saturated solution; (3) there should, if possible, be no loss in the quantity of the saturated solution as a result of the measurement.

The densities and electric conductivities of saturated solutions have been investigated by the authors with a view to determining transition temperatures. The density measurements were carried out with the saturated solution of sodium sulphate. The curves obtained by plotting the density intersect at a wide angle at 32·4° corresponding to the transformation of the decahydrate into the anhydrous salt at this temperature.

Conductivity measurements were also carried out with this salt; as in the case of the density, two curves intersecting at about 32·5° were obtained.

The change in direction of the curve at this temperature is not so great as was expected; this, is, however, explicable on the ground that the solutions are so concentrated.

A second series of experiments was carried out with thorium sulphate, the nonahydrate of which, according to Roozeboom, changes into the tetrahydrate at about 43°. The concentration of the saturated solution at the transition-temperature is, in this case, only about one-third normal.

On plotting the conductivity on a diagram, two curves are obtained intersecting at about 48°. To confirm this result, the transition temperature has been determined dilatometrically and tensimetrically, by which methods 46·5° and 47·5° were obtained. Roozeboom's determination of 43° would therefore appear to be somewhat too low. The authors point out the availability of the above methods of determination in cases where other methods cannot be used with advantage.

149. "*Constitution of Amarine, of its supposed Dialkyl- and Diacyl-derivatives, and of Isoamarine.*" By Francis R. Japp, F.R.S., and James Moir, M.A., B.Sc.

The author's find that Claus and Elbs's "dibenzylamarine" (m. p. 139—140°) has in reality the composition represented by the formula $C_{21}H_{18}(C_7H_7)_2N_2O$, and is *benzoyl*-s-*dibenzyl* i-*diphenylethylenediamine*,—

$$\begin{array}{l} C_6H_5\cdot CH\cdot N(C_7H_7)\cdot CO\cdot C_6H_5 \\ \quad\quad | \\ C_6H_5\cdot CH\cdot NH\cdot C_7H_7 \end{array}$$

It may be obtained, along with a dibenzoyl-derivative (m. p. 268°), by the action of benzoic chloride on Grossmann's *s*-dibenzyl-*i*-diphenylethylenediamine, thus proving its constitution. This dibenzoyl-derivative, melting at 268°, may also be obtained by introducing a benzoyl-group into "dibenzylamarine." Claus and Elbs's "dimethylamarine" (m. p. 146°) is in reality the corresponding *benzoyl* s-*dimethyl*-i-*diphenylethylenediamine*, and Borodine's "diethylamarine" (m. p. 110—115°; the authors find 125°) is the corresponding diethyl-derivative.

When benzoyl-*s*-dibenzyl-*i*-diphenylethylenediamine hydrochloride is heated to 220°, it parts with water, yielding dibenzylamaronium chloride,—

$$\begin{array}{l} C_6H_5\cdot CH\cdot N(C_7H_7)\cdot CO\cdot C_6H_5 \\ \quad\quad | \\ C_6H_5\cdot CH\cdot N^{v}(C_7H_7)H_2Cl \end{array} =$$

$$= \begin{array}{l} C_6H_5\cdot CH\text{——}N(C_7H_7) \\ \quad\quad | \quad\quad\quad\quad \diagdown \\ C_6H_5\cdot CH\cdot N^{v}(C_7H_7)Cl \quad\quad C\cdot C_6H_5 \end{array} + H_2O,$$

a reaction which proves conclusively the constitution of the dialkylamaronium salts.

Dibenzylamaronium chloride gives a dichromate of the formula $(C_{35}H_{31}N_2Cl)_2,H_2Cr_2O_7$ (m. p. 173°), which, when boiled with glacial acetic acid and a little hydrochloric acid, yields *dibenzyllophonium chloride*, showing that the latter substance has the constitution—

$$\begin{array}{l} C_6H_5\cdot C\text{——}N(C_7H_7) \\ \quad\quad || \quad\quad\quad\quad \diagdown \\ C_6H_5\cdot C\cdot N^{v}(C_7H_7)Cl \quad\quad C\cdot C_6H_5, \end{array}$$

instead of, as suggested by Japp and Davidson,—

$$\begin{array}{l} C_6H_5\cdot C\cdot N^{v}(C_7H_7)_2Cl \\ \quad\quad || \quad\quad\quad\quad \diagdown \\ C_6H_5\cdot C\text{———}N \quad\quad C\cdot C_6H_5. \end{array}$$

The authors regard amarine as 2-*phenyl*-4 : 5-cis-*diphenyl*-4 : 5-*dihydroimidazole*,—

$$\begin{array}{l} \quad\quad H \\ C_6H_5\cdot \dot{C}\cdot NH \\ \quad\quad | \quad\quad\quad \diagdown \\ C_6H_5\cdot C\text{—}N \quad\quad C\cdot C_6H_5, \\ \quad\quad \dot{H} \end{array}$$

employing the numbering of the imidazole ring adopted by M. M. Richter. A formula identical with the foregoing, excepting that the configuration was not indicated, was put forward by Claus.

Amarine is thus a meso-form derived from Grossmann's *i*-diphenylethylenediamine (m. p. 120—121°), which this author obtained by the reduction of amarine.

The authors show that Snape and Brooke's isoamarine is 2-*phenyl*-4 : 5-trans-*diphenyl*-4 : 5-*dihydroimidazole*—the corresponding racemic form. With Professor Snape's permission, they reduced isoamarine with sodium in boiling alcohol, and obtained, as in Grossmann's analogous experiment with amarine, a benzylidene derivative, which on hydrolysis with acids, gave benzaldehyde and a base—in this case Feist's *r*-diphenyl-

ethylenediamine (m. p. 90—92°). Isoamarine is thus related to Feist's base, in the same way as amarine to Grossmann's. Feist's base (prepared by the reduction of α-benzildioxime), when heated with benzoic acid at 170—180°, yielded isoamarine, thus confirming the foregoing view as to the constitution of the latter compound. Amarine benzoate undergoes no change at this temperature.

Isoamarine may be readily prepared by fusing amarine with sodium, or by heating amarine hydrochloride above its melting-point.

The authors find that Claus and Scherbel's supposed dibenzoylamarine is identical with Grossmann's *s*-dibenzoyl-*i*-diphenylethylenediamine, and that Bahrmann's supposed diacetylamarine is acetylbenzoyl-*i*-diphenylethylenediamine. This removes the supposed evidence for the symmetrical or di-imidic formula of amarine.

The authors have made a detailed study of the reactions of the supposed dibenzylamarine, the results of which confirm the foregoing views as to its constitution.

150. "*The Atomic Weight of Nitrogen.*" By G. Dean, B.A.

The work of which an account is given in this paper is in continuation of that of which a preliminary notice has already been communicated to the Society (*Proc.*, 1898, xiv., 174). After giving a summary of the results of previous workers, the author deduces a mean value from them of 14·034 for the atomic weight of nitrogen, but points out that the means of the determinations by chemical methods of individual workers vary from 13·975 (Pelouze) to 14·05 (Stas). The ratio of the densities of oxygen and nitrogen as determined by Lord Rayleigh and by M. Leduc is 16 : 14·003. These variations seemed to be too great, so it was thought that it would be both important and interesting to try a new method which would involve as few atomic weights as possible, and only those which are known with the highest accuracy. Silver cyanide was selected as the compound containing nitrogen, and the ratio between a given mass of it and that of the potassium bromide required for the complete precipitation of the silver contained in it determined with all the precautions insisted on in such work by Stas. The cyanide was decomposed in some cases by dissolving it in nitric acid, in other experiments sulphuric acid. The ratio between the purest silver and the sample of potassium bromide used was carefully determined, so that the ratio found was really Ag : AgCN. This was found to be 107·93 : 133·962, whence CN = 26·032 and N = 14·031 if C = 12·001.

ROYAL INSTITUTION.

General Monthly Meeting, December 4th, 1899.

Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members:—Professor H. E. Armstrong, F.R.S., and Messrs. J. H. Bowman, J. S. Brookfield, J. B. Carrington, W. B. Cloete, and L. Leigh Smith.

The following letter from the Clerk of the Goldsmiths' Company was read:—

"Goldsmiths' Hall, London, E.C., November 16th, 1899.

"Dear Sir,—

"I am directed to inform you that the attention of the Court of the Goldsmiths' Company having been drawn to the fact that the Royal Institution of Great Britain has lately celebrated its Centenary, they have, in order to mark their sense of the importance of that event, been pleased to make to the Institution the further grant of £1000, for the continuation and development of original research, and especially for the prosecution of further investigations of the properties of matter at temperatures approaching that of the absolute zero of temperature.

"I enclose a cheque for this amount, and I shall feel obliged to you to acknowledge the receipt.—I am, dear Sir, Your obedient Servant,

(Signed) Walter S. Prideaux.

"The Hon. Secretary,
The Royal Institution of Great Britain."

The following resolution (proposed by the Lord Chancellor and seconded by Sir A. Noble) was then passed:—

"That the Members of the Royal Institution of Great Britain, in General Meeting assembled, having been informed that the Court of the Goldsmiths' Company have made a donation of £1000 to the funds of the Royal Institution in commemoration of its Centenary, and in aid of the investigations which are being carried on in its Laboratories into the properties of matter at low temperatures, desire to express to the Court their profound and grateful appreciation of this second munificent manifestation of their practical interest in the work of the Institution — a manifestation which has been made on this occasion at once reminiscent of past services to science and prescient of services yet to come."

NOTICES OF BOOKS.

Science Sketches. Chemistry, its Evolution and Achievements. By Ferdinand G. Wiechmann. New York: William R. Jenkins. 1899. Pp. viii.—176. 16 mo.

Dr. Wiechmann, who is already known to chemists by his works on Sugar Analysis and Theoretical Chemistry, now offers a modest volume that attempts to enlist the interest of non-professional readers in an exact science. He sketches the history of chemistry from its obscure birth through the ages down to the present time, following somewhat the same lines as those of Hermann Kopp, and narrates—briefly of course—the most notable achievements of the science in its technical applications. The work is not divided into chapters, but marginal notes in full-faced type serve the same purpose.

It is ungenerous to point out omissions in a work of 176 pages, the subject of which covers such an enormous field; it is more just to give credit for inclusions than to criticise exclusions. The Index of Names has a good feature; each name in the alphabetical list bears the birth-date and death-date of the person. In the list of works consulted we miss the grand volumes by Berthelot ("Collection des Alchemistes Grecs," and "La Chimie au Moyen Age").

Whether the author has really succeeded in portraying the "grandeur and the charm of the science" in such a fashion as to attract non-professional readers, can but be determined after the book has been some time before the public; his attempt is praiseworthy, yet many paragraphs can only be appreciated by the educated chemist already familiar with the growth of the science.

The primary caption of the title page, "Science Sketches," intimates that this book is the first of a series, but the preface makes no allusion to this.

Index to the Literature of Zirconium. By C. Langmuir and Charles Baskerville. Smithsonian Miscellaneous Collections, 1173. Washington City: Published by the Smithsonian Institution. 1899. 29 pp. 8vo.

This "Index" was begun independently by the two authors, who live one thousand miles apart; an announcement in the "Fourteenth Annual Report of the Committee on Indexing Chemical Literature" (appointed by the American Association for the Advancement of Science

in 1882) directed the attention of one of the chemists to the undertaking begun by the other, and after correspondence they wisely joined forces and produced the present booklet. It bears the endorsement of the Committee just named, and forms one of the series that now embraces the following elementary substances:—U, Mn, Ti, Vd, Cb, Di, Ce, La, Pt, Pd, Ir, Rh, Os, Ru, and Tl, besides many other topics. The first-named and the last ten have appeared in the publications of the Smithsonian Institution.

The bibliography of zirconium begins with the discovery by Klaproth in 1789, and is brought down to the end of the year 1898; the total number of references being 248, exclusive of reproductions and abstracts.

All publications by the Smithsonian Institution, of Washington, D.C., are for sale at low prices, merely to cover printing and paper. The agents of the Institution for Great Britain are Messrs. Wesley and Son, 28, Essex Street, Strand, London. H. C. B.

The Chemistry of Soils and Fertilisers. By Harry Snyder, B.Sc. Easton, Pa. 1899, Pp. 277.

The proper use of manures is a problem which is by no means yet thoroughly worked out and understood: as our knowledge of chemistry advances we know more and more what a manure should be, and that organic nitrogen is the predominant constituent required. It has already been pointed out by Sir William Crookes that the yield of wheat depends, to a very great extent, on the amount of nitrogen in the soil: this subject must not be lost sight of, and we are glad to see that Mr. Snyder fully recognises the importance of the question.

He treats the whole matter in a thorough manner from the time of De Saussure, Davy, and Boussingault, to the present time. The long-continued experiments of Gilbert and Lawes receive due attention, as also do those of Ville: we are, however, sorry to see that in spite of political approachments England and the United States are slowly but surely drifting apart. This book is written, not in the English, but in the American language.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 20, November 13, 1899.

Preparation and Properties of Crystalline Phosphides of Strontium and Barium.—A. Jaboin.—By means of the electric furnace, the author has prepared crystalline phosphides of strontium and barium. The corresponding phosphates are reduced by means of carbon. Analysis shows these two bodies to have the composition P_2Sr_3 and P_2Ba_3. They are very stable, but possess great chemical activity. They decompose water at ordinary temperatures, giving phosphoretted hydrogen and the hydrate of barium or strontium.

Estimation of Phosphorus in Organic Compounds.—Ch. Marie.—In the course of researches on organic compounds containing phosphorus, the author finds that the employment of potassium permanganate in nitric solution to oxidise the phosphorus is not satisfactory. He therefore modifies the method by dissolving the substance to be analysed in excess of strong nitric acid and adding the permanganate little by little. This method has been compared with the ordinary method of oxidation in sealed tubes, and is found to give much better results, even in the case of compounds very difficult to oxidise, such as ammoniaco-calcic aceto-diphosphite.

New Asymmetric Compounds of Nitrogen obtained by Synthesis and possessed of Rotatory Power.—W. J. Pope and S. J. Peachey.—(See p. 252).

MEETINGS FOR THE WEEK.

Monday, 11th.—Society of Arts, 8. (Cantor Lectures). "Enamellin upon Metals," by Henry Hardinge Cunynghame.
Wednesday, 13th.—Society of Arts, 8. "Sea Angling and Legislation," by F. G. Aflalo.
Thursday, 14th.—Society of Arts, 4.30. "Round about the Andamans and Nicobars," by Colonel R. C. Temple, C.I.E.

THE
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OF
THE ROYAL INSTITUTION.

Directors:
The Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S.
Professor DEWAR, M.A., LL.D., F.R.S.
Superintendent of the Laboratory:
Dr. Alexander Scott, M.A., D.Sc., F.R.S.

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All persons desiring to be admitted as Workers must send evidence of scientific training, qualification, and previous experience in original research, along with a statement of the nature of the investigation they propose to undertake.

Michaelmas Term.—Monday, October 2, to Saturday, December 16.
Lent Term.—Monday, January 8, to Saturday, April 7.
Easter Term.—Monday, April 30, to Saturday, July 28.

Forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2090.

GOLD-ALUMINIUM ALLOYS.*

By C. T. HEYCOCK, F.R.S., and F. H. NEVILLE, F.R.S.

THE first part of this paper gives the equilibrium curve for the liquid alloys and the various solid bodies that can form in them. The curve is based on the determination of the freezing points of mixtures varying in composition from pure gold to pure aluminium.

The freezing points were determined by means of platinum resistance pyrometers of the Callendar-Griffiths type, and the composition of each alloy was found by extracting a sample from the crucible and analysing it.

The ordinate in the curve is the freezing point on the air-centigrade scale, and the abscissa is the composition of the alloy expressed in atomic percentages of aluminium.

The curve was found to consist of seven branches, each branch corresponding to a state in which a particular solid crystallises first. In harmony with this, seven substances can be detected in the solid alloys. The bodies are:—

Gold; Au_4Al; Au_5Al_2 or perhaps Au_8Al_3; Au_2Al; a body which is probably AuAl; $AuAl_2$, Roberts-Austen's purple alloy; aluminium.

The bodies Au_2Al and $AuAl_2$† are indicated by well-marked summits in the curve, at 33·4 and at 66·6 atomic per cents. of aluminium respectively.

The melting or freezing point of Au_2Al is at 625° C., that of $AuAl_2$ is at 1062° C., apparently identical with the melting point of gold itself. The body whose formula we give as either Au_5Al_2 or Au_8Al_3 has its melting point at 575° C. The body Au_4Al has its melting point near 550° C. That of the hypothetical AuAl is not given by the curve.

The curve has three well-marked eutectic angles. One of these is at 527° C. and 3·6 per cent by weight of aluminium, the alloy here being a mixture of Au_4Al and Au_5Al_2. The next is at 569° C. and 8·36 per cent by weight of aluminium; this alloy has a composition corresponding to the formula Au_3Al_2, but it is a mixture of Au_2Al and AuAl. The third eutectic is at 648° C., and the alloy contains 1·87 per cent by weight of gold; it is a mixture of $AuAl_2$ and aluminium. We see from the above that the mixture with the lowest melting point of all is that containing 3·6 per cent by weight of aluminium, this small percentage depressing the melting point of gold from 1062° C. to 527°, that is more than 500°. A liquid of this composition, though almost wholly composed of gold, will not begin to solidify until this comparatively low temperature of 527° C. is reached.†

Each of these eutectic points gives rise to a horizontal row of second freezing points in the curve, and the alloys containing more than 44 and less than 60 atomic per cents of aluminium have three distinct freezing points corresponding to the successive formation of three solid bodies.

The four compounds, Au_4Al, Au_5Al_2, Au_2Al, and the hypothetical AuAl, are pure white substances. $AuAl_2$, as is well known from the work of Sir W. Roberts-Austen, is a magnificent purple body.

The latter part of the paper gives the result of a microscopic examination of polished and etched sections of alloys taken from various parts of the curve. All the bodies referred to above could be distinguished under the microscope. The photomicrographs accompanying the paper show that the structure of the solid alloy is everywhere in strict harmony with the indications of the freezing point curve. Speaking generally, we may say that the patterns observed in the photographs repeat themselves at corresponding points of each branch of the curve. For example, near the summit of the branch corresponding to the pure alloy, Au_2Al, the photograph shows us more or less hexagonal polygons of this substance almost entirely filling the field, and only separated from each other by very fine lines of impurity. If we take a section of an alloy a little way below the summit, we see the polygons of Au_2Al surrounded by a ribbon-like network of mother substance. Still further down, the crystals of Au_2Al are scanty, and arranged in such regular patterns, generally in lines at right angles to each other, as to render it certain that they crystallised freely while surrounded by liquid. Finally, at the bottom of the branch, that is at the eutectic point, the large crystals of Au_2Al are absent, and the whole field is full of the mother substance, which is sometimes but, as we explain in the paper, not always a eutectic mixture.

If, leaving the eutectic point, we ascend the next branch, these phenomena repeat themselves, but the primary crystallisation (that is the matter which solidified first) is now of a different substance.

Some of the photographs of alloys very rich in aluminium were taken by the Röntgen rays, and an enlargement made from the negative. The contrast between the Röntgen ray photograph and the surface photograph of the same alloy shows what a much better picture of the structure of the alloy is given by the Röntgen rays.

* Abstract of a Paper read before the Royal Society, Dec. 7, 1899.

† The rapid depression in the freezing point of gold, due to the presence of small quantities of aluminium, and the great rise in the freezing point as the composition corresponding to the compound $AuAl_2$ is approached, have been already discovered by Sir William Roberts-Austen.

ATOMIC WEIGHT OF THE METAL IN RADIFEROUS BARIUM CHLORIDE.

By Madame SKLODOWSKA CURIE.

M. CURIE, M. Bémont, and I have already published a research, in the course of which we showed that the barium compounds extracted from uranium mineral possessed great radio-activity. We also stated that we believe this activity to be due to a new element—radium.

The barium salts extracted from uranium minerals are only distinguished from barium salts from other sources by their radio-activity. The lines of barium are seen with the spectroscope, and the atomic weight agrees with that of barium.

By fractionation it is possible to concentrate the radio-activity so as to obtain more and more active products.

M. Demarçay has studied the successive fractions spectroscopically. He was able to discover a new spectrum in the latter fractions, some of the lines attaining the same intensity as the barium lines.

I have determined the atomic weight of the metal in successive fractions, and I find that the atomic weight of strongly radio-active barium is greater than that of ordinary barium, and that the difference increases with the activity.

I fractionally crystallised 2 kilos. of purified radiferous barium chloride, which was extracted from half a ton of residue from uranium mineral. This treatment concentrated the radio-activity in the least soluble parts. I then obtained several fractional precipitations with alcohol from the most active portion; the activity concentrates in the precipitated portions.

The radiferous barium chloride so obtained is treated with sulphuretted hydrogen to eliminate the small quantity of lead present; after this it contains no further perceptible impurity.

I determined the atomic weight of the metal by esti-

mating the chlorine in the anhydrous chloride by silver nitrate. The weight of chloride used was about 0·5 grm.

Each determination of the atomic weight of the metal in the active chloride was accompanied by a control experiment on inactive barium chloride.

The activity of the barium chloride before fractionation was about sixty times greater than that of uranium, but to obtain a difference in atomic weight, it was necessary to have an activity several thousand times greater than that of uranium.

In the following table, i denotes the electric current which the active barium chloride produces when it occupies a circular surface of 2 c.m. diameter at the centre of one of the plates of a condenser of the following dimensions:—Diameter of plates, 8 c.m.; distance between plates, 3 c.m.; difference of potential between the plates, 100 volts. The current which metallic uranium gives under these conditions is equal to $0{\cdot}25 \times 10^{-11}$ ampères. a Denotes the radio-activity of the active chloride, that of uranium being taken as 1. m Denotes the atomic weight of the metal in the radio-active chloride; and Ba, the atomic weight found for barium in the control experiment.

i (10^{-11} ampères).*	a.	m.	Ba.
750	3000	140·0	138·1
1170	4700	140·9	137 6
1870	7500	145·8	137·8

* In the original this reads 10^{+11} ampères, which must be a mistake for 10^{-11}.

There is seen to be a very decided difference between the atomic weight of barium and that of the last fraction.

The radiant properties of each specimen were measured directly after preparation in a dry state. Indeed, the radio-activity of all the radiferous chlorides of barium increases considerably for several days after passing from solution into the solid state, whether by crystallisation (chloride) or by precipitation (sulphate, carbonate). This activity seems to reach a limiting value by the end of some weeks, which, for very active compounds, may be five or six times as great as the initial value.

The specimen of which the spectrum was described by M. Demarçay started with $a = 17{,}000$. I had not enough of this left for an atomic weight determination.

Both my experiments and the spectrum examination seem to prove that the hypothetical element which we have called radium does, indeed, exist, and that it possesses an atomic weight slightly higher than that of barium.—*Comptes Rendus*, cxix., No. 20.

RELATIONS BETWEEN THE ATOMIC WEIGHTS AND PHYSICAL PROPERTIES OF ELEMENTS.

By THOMAS BAYLEY.

The following facts, which show a connection between the atomic weight and certain physical properties of the elements, have not been recorded, as far as I am aware.

The product of melting-point (absolute) × coefficient of linear expansion is approximately a constant for certain elements. For Cd it is 0·0197, for Zn 0·0205, for Cu 0·022, for In 0·020, for Pd 0·021, for Ir 0·0193, for Pt 0·018, for Bi 0·0216, for Au 0·0196. The product is somewhat higher for these:—Mg 0·024, Ag 0·024, S 0·025, Na 0·026, K 0·028.

Taking the products as equal, then two cubes of (say) Zn and Cd, of equal dimensions at absolute zero, will have equal volumes at the respective melting-points. The weights of the cubes are as sp. gr. Cd : sp. gr. Zn, and the number of atoms in each as—

$$\frac{\text{Specific gravity Cd}}{\text{Atomic weight Cd}} : \frac{\text{Specific gravity Zn}}{\text{Atomic weight Zn}}$$

Dividing the expansion among the atoms to obtain the atomic expansion (absolute zero to melting-point), we get—

$$\frac{\text{Expansion}}{\frac{\text{Specific gravity}}{\text{Atomic weight}}} = \frac{\text{(Atomic weight) Expansion}}{\text{Specific gravity}} =$$

Atomic volume × Expansion. The expansion is directly as the atomic volume.

Again,—

Specific heat × melting-point (abs.) × atomic weight = atomic heat (absolute zero to melting-point).

Let—

$$\frac{\text{Specific heat} \times \text{melting-point}}{\text{Atomic weight}} = x,$$

then—

Specific heat × melting-point = x atomic weight,

and by substitution—

Atomic heat (absolute zero to melting-point) = x (atomic weight)^2.

The values of x are for—

K = 1·415	Au = 0·2172	N = 0·997	Ga = 0·3426
Na = 4·372	Ag = 0·6425	P = 2·066	Zn = 1·01
	Cu = 2·02	Sb = 0·394	Cu = 2·02
		Bi = 0·0796	

In = 0·2246	Hg = 0·03725	Pt = 0 335
Ag = 0·6425	Au = 0·2172	Pd = 1·01

It will be observed that, in Group I., the value of x for K is closely approximate to one-third of the value for Na, the value for Au is one-third that for Ag, the value for Ag is one-third that for Cu. The values of x for Group V. are for N = ½ P, for Sb = ⅕ P, Bi = ⅕ Sb. Similarly, x for Zn = ⅛ Cu, for Ga = ⅓ Cu, In = ⅔ Ag, Hg = ⅛ Au, Pt = ⅓ Pd. Of course, specific heat varies with temperature, but a similar consideration applies to Dulong and Petit's law of atomic heats.

December 6, 1899.

AMMONIUM MOLYBDATE AS A DELICATE REAGENT FOR STANNOUS CHLORIDE.

By J. P. LONGSTAFF.

Fresenius, in his "Qualitative Analysis" (English translation, 10th edition, p. 184), says that the hydrochloric acid solution of molybdic acid is coloured "immediately on addition of stannous chloride, the colour being brown, green, or blue, according to the proportion of reducing agent and the concentration of the solution." This reaction is the basis of a well-known test for molybdic acid, and is given among the reactions of molybdates in text-books of qualitative analysis. So far, however, as I have been able to ascertain after careful search, it does not appear that molybdic acid has ever been proposed as a reagent in testing for stannous chloride; and this seems very remarkable, as I find that ammonium molybdate (the ordinary laboratory reagent) is not only a suitable reagent, but that, for very dilute solutions of stannous chloride, it affords a much more delicate test than mercuric chloride does. I think, therefore, that it may be useful if I give the main results I have arrived at.

The solutions tested were prepared by dissolving small quantities—varying from 7 m.grms. to 4 c.grms.—of pure tin (as supplied by Harrington) in hot concentrated hydrochloric acid, and at once diluting to a litre or other suitable definite volume. Measured quantities were drawn off by a pipette and at once diluted, and, in this way, solutions of various concentrations, but all containing very small quantities of tin, were obtained. It was found necessary to carry through each experiment as rapidly as possible,

since very dilute stannous solutions undergo oxidation in a remarkably short time. For instance, in my first experiment, ordinary distilled water was used, and the solution, which contained 0·0230 grm. of tin in a litre, gave no indication of the presence of stannous chloride at the end of half an hour. The oxidation had evidently been effected by means of air dissolved in the water. In subsequent experiments recently boiled-out water was always employed.

By using all reasonable precautions to prevent oxidation, I find that, for ordinary test-tube work, the addition of ammonium molybdate to, say, 10 c.c. of a stannous chloride solution, of a dilution corresponding to 1 part of tin in anything up to 100,000 parts of solution, gives a very distinct blue colouration.

The delicacy of the test is, however, much greater than this. For instance, 0·0103 grm. of tin dissolved in hydrochloric acid was diluted to 100 c.c.; 1 c.c. of this solution, when diluted with 150 c.c. of water, still gave a perceptible colouration with ammonium molybdate. This corresponds to a dilution of 1 part of tin in 1,500,000 of solution. The presence of the blue colour was rendered distinct by placing the beaker containing the solution and reagent beside another containing only water and reagent, the two liquids being of equal volume; when a sheet of white paper was held behind the beakers, the difference in colour of the liquids was rendered perfectly distinct.

Solutions of greater dilutions than the last mentioned were not prepared.

If, in laboratory practice, the tin is separated from the other metals of the arsenic group by reduction with zinc and hydrochloric acid, the zinc with the tin deposit upon it should be carefully washed with water, completely dissolved in concentrated hydrochloric acid, and the solution so obtained diluted with water. Ammonium molybdate should then be added, and, if tin is present, even in very minute quantity, a distinct blue colour will appear. This colour, which slowly disappears on exposure to the air, is at once discharged by the addition of concentrated hydrochloric acid. Hence a strongly acid solution must always be diluted before applying the test.

Pure zinc deposits tin very slowly, so that, in order to get down enough to give a distinct reaction with mercuric chloride, when it is dissolved in hydrochloric acid, the process of reduction must be allowed to go on for a considerable time; but this is not necessary when ammonium molybdate is to be used as the test reagent, since a trace of tin, which will give no visible precipitate with the former, gives at once a perfectly distinct colouration with the latter.

Of course, whether the zinc to be used be "pure" or not, a quantity of it should be completely dissolved in hydrochloric acid, and, after dilution, the liquid should be examined for tin in the way I have indicated. If this is found to be present, of course such zinc is absolutely useless for the purpose of analysis.

So far as my experience goes, laboratory students have great difficulty in conclusively proving the presence or absence of tin, in a complex mixture, by the ordinary methods of qualitative analysis. In the method ordinarily employed, the sulphides of antimony and tin (always SnS_2 after treatment with yellow ammonium sulphide and reprecipitation) are boiled up with strong hydrochloric acid, the solution is evaporated to get rid of most of the acid, and is then diluted with water. Platinum foil and zinc, in contact, are then used to precipitate antimony and tin. As previously pointed out, however, the tin comes down very slowly, and, when it is (with the zinc) dissolved in hydrochloric acid, and the solution concentrated to a very small bulk, it is frequently found that mercuric chloride gives no precipitate whatever, and sulphuretted hydrogen only a trace of precipitate or a faint colour, either of which may be caused by a small quantity of antimony. Now, neither arsenious chloride nor antimonious chloride gives a blue colour with ammonium molybdate; and therefore I venture to say that this reagent will, on taking the precautions already pointed out, indicate with ease and certainty the presence or absence ol tin.

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REMINISCENCES OF BUNSEN AND THE HEIDELBERG LABORATORY, 1863—1865.*

By HENRY CARRINGTON BOLTON, Ph.D.

I FIRST met Bunsen in the lovely, retired valley of Engelberg, Switzerland, during the summer of 1863; I had spent the preceding twelve months in Paris, working in Dumas's laboratory at the Sorbonne, and in the Ecole de Médecine under Wurtz, and was expecting to continue my studies in Heidelberg. Learning by accident that Bunsen was at an adjoining *Gasthaus*, I called on him and told him of my plans; he received me graciously, and immediately won my heart by his affability, by the charming smile that lit up his large features, and by his unselfish interest in my personal affairs. Being myself quite ignorant of the German language we conversed in French, and he gave me useful hints as to the opening of the University laboratory.

My first *semester* at Heidelberg was devoted almost exclusively to laboratory work, but I attended Bunsen's lectures on general chemistry every morning at nine o'clock in the adjoining auditorium. Bunsen's habit of saying one word when he meant to use another was at first puzzling, particularly as I was very weak in German, but when he exhibited the violet vapour of iodine and called it chlorine my previous knowledge of chemistry assisted comprehension. After every lecture Bunsen rarely missed spending several hours in the laboratory, going from student to student with enquiries, suggestions, and useful hints. Desirous of securing my share of this personal contact, I soon found the best way to induce the Hofrath to linger was to have a supply of clean test-tubes and beakers on an orderly desk, with a query or two requiring experimental answers. Any suggestion as to the use of the spectroscope in connection with a substance under examination was sure to interest the Professor, as that famous instrument was a comparatively new adjunct to chemical work, being then about four years old.

When in the laboratory Bunsen habitually carried between his lips a short, unlighted cigar, and he often stopped at a student's desk only long enough to light the tobacco at a "Bunsen" burner; in a few minutes the cigar was again without a spark owing to his absent-minded neglect to pull on it. Absent-mindedness was a marked trait in Bunsen's character, and many amusing anecdotes are told of the difficulties it brought him. The statement that he remained a bachelor because he forgot his wedding-day is, of course, apocryphal, as is the other about his putting on a suit of garments on top of others that he had forgotten to take off; but the following came under my personal observation. Bunsen used to dine every day at a little table reserved for him in a restaurant connected with the hotel in which I lived; one spring he fell into the habit of ordering veal-cutlets and asparagus as the chief item for his meal, and, without reflection or feeling that a change of diet would be agreeable, he continued to order "*Kalbs-cotelette und Spargel*," daily for several weeks, until one day the *Kellner* gravely informed him that asparagus was no longer in season and could not be supplied. Bunsen seemed to be immensely taken aback, and to realise for the first time that he had been dining on one dish for a long period; he soon recovered himself, however, and asked the waiter for the bill-of-fare, from which, after careful examination. he ordered mutton-

* Advance proofs from *Science*.

chops and pease, and this was his daily diet up to the time I changed my hotel.

When the laboratory was closed for the Christmas holidays I tried to get permission to work in the deserted rooms, but in vain, and not wishing to be idle I worked at growing crystals, improvising a desk out of a hotel wash-stand, and a heater out of the huge porcelain stove. Some time after I showed to Bunsen a single crystal of copper-calcium acetate about 3 inches long, with perfectly regular facets, and of which I was quite proud; he looked at it rather solemnly, as I thought, and enunciated the single word "*ausgezeichnet*." This was not in my limited vocabulary, and whether a commendation or a disapproval I could not divine; I puzzled over the word all day, and on returning home the dictionary explained its meaning to my great satisfaction.

As my knowledge of German increased I attended the lectures of Kirchhoff and of Kopp, but I never was able to *enjoy* the latter's interminable sentences and involved style.

Bunsen's assistants in the laboratory at the time of my sojourn were Dr. Bender and Dr. Rose; the latter had the reputation among the students of giving more accurate instruction in mineral analysis than Bunsen himself. Rose is now professor in the University of Strassburg.

Bunsen's methods in mineral analysis were not wholly approved of by the students; one day he stopped at my desk for a moment, and picking up a filter containing a moist precipitate he inquired: "What have you here?" Seeing with consternation a portion of my *quantitative* precipitate sticking to his thumb, I hastily seized a "*Spritz-flasche*," and washed the substance off his thumb into the filter on the funnel before venturing a reply. Bunsen smiled genially and passed on to my neighbour.

Bunsen showed extraordinary callousness to heat, being able to hold in his fingers metal nearly red hot; on one occasion when stirring a glowing crucible with a very short spatula, his skin fairly sizzled and for relief he took hold of the lobe of his ear with his smoking thumb and fore-finger, explaining that the ear was the coolest part of the body.

The celebrated Dr. C. R. Fresenius, of Wiesbaden, having appropriated some discovery or method of Bunsen, without giving credit, was cordially disliked by him, and he once showed it by a significant act. A student accosted the Hofrath as he passed by and put to him some simple question in analytical chemistry; on the desk lay open a copy of Fresenius's "*Anleitung*," whereupon Bunsen closed the book with a deprecatory gesture, pulled out the drawer of the student's desk to its extreme limit, and thrust into it as far back as possible the objectionable volume, saying: "*Nun, mein Herr*, we will proceed."

Bunsen was rather sensitive to criticism; one of my American colleagues tells me of an incident illustrating this. The professor proposed to the student the joint preparation of certain cæsium and rubidium salts, saying he would secure several barrels of the mineral water rich in the chlorides, and would have the water boiled down to a small volume ready for the separation of the rare elements. The American felt highly pleased at the flattering proposal, and to show his interest in the matter mentioned that he had studied under Professor O. D. Allen, of New Haven, who had done work on cæsium and rubidium. This was an unfortunate remark, however, for Allen had corrected Bunsen's figures for the atomic weight of Cs, and the Hofrath remembering this never again mentioned the subject to my friend.

In those days students were obliged to prepare some substances now commonly provided, and to construct some apparatus with their own hands. Every student had to etch and calibrate his own eudiometer, and some of them wasted much time over the hydrofluoric acid process before getting good results. I remember, too, purifying potassium hydroxide by solution in alcohol (an extra charge), and evaporation in a large silver basin loaned by an assistant. One green, Russian student bought at Desaga's, potassium cyanide instead of the hydroxide, and was vainly trying to dissolve it, walking about the laboratory shaking the bottle for hours, when Bunsen noted its singular appearance, caused the operation to be suspended, and on ascertaining the nature of the substance cautioned the student against it.

Speaking of Russians reminds me of an amusing occurrence: one of them was instructed to precipitate a substance "*mit überschüssigem Kali* and not finding any bottle labelled "*überschüssiges Kali*," he inquired for it of a neighbour, who mischievously sent him to Dr. Bender, telling him the article was kept under lock and key with other costly substances, such as silver nitrate and platinum chloride. The astonished assistant explained to the Russian that an *excess* of potash did not require a special bottle; the student was nicknamed "*Uberschussiges Kali*" for the rest of the *semester*.

Many nationalities were represented in Heidelberg laboratory; besides Russians there were Bessarabians, Hollanders, Bohemians, Germans from North and from South, Austrians, one Chilian, one Englishman (the late Dr. Walter Flight, F.R.S.), one Scotchman (Mr. Sims), one Irishman (Mr. John Price), and several Americans, fifty-nine students in all, of which fifty-eight were incessantly smoking; the fumes of tobacco mingled with vapours of H_2S, SO_2, HNO_3, and NH_3, making an atmosphere so thick that I regret not having cut off a slice as a souvenir.

The students, from time immemorial, had a voluntary organisation to maintain order in the laboratory; they elected at the beginning of each *semester* an officer known as "*Polizei-Diener*," who was authorised to impose small fines for petty offences, the money thus secured being devoted at the end of the term to the purchase of books for the small library placed on shelves in the balance-room. This custom I understand still obtains. At the opening of my third term I was elected "*Polizei*," and duly instructed in my duties; being watchful and courageous I collected more money during my term of office than had been added to the library fund for many years. The misdemeanours for which fines were imposed were:—Leaving an unused gasburner lighted, failure to resort to the "*Stink-Zimmer*" when noxious gases were generated, failure to replace bottles or apparatus used in common, and leaving a balance door open or weights on the pans, which latter was accounted a very heinous offence; the fines ranged from six kreutzers (Baden) to half a gulden. My official life was marked by two events that greatly excited and amused the whole laboratory; one of the events was regarded as an exhibition of unparalleled audacity, of which only an American was capable—I fined Hofrath Bunsen! The Professor, after lighting his cigar at the flame of a Bunsen burner, left the gas burning and went out of the room; according to custom, and to the consternation of the students, I chalked on the desk that Bunsen had used, the words "six Kr." over my initials, a notice that could not be erased until the fine was paid. Next day when Bunsen approached the desk, he glanced at the inscription, smiled broadly, and, to the amusement of the crowd of students that had gathered to see the result of my daring, opened his purse and handed me the six kreutzers with a pleasant commendation of the fidelity of the "*Polizei*."

The other event concerned a very close-fisted American whose numerous fines I was unable to collect; when they reached the enormous sum of one and a half gulden (about 2*s*. 5*d*.), I consulted some of the older German students, stating the facts and asking for advice. They declared they had never heard of such a case, and they authorised me to confiscate some chemical apparatus belonging to the American and to sell it at auction. I secured a fine beaker glass, the outside one of a large nest, and after due notice, amid the shouts of the fifty-nine students gathered in the lecture-room, the beaker was sold at auction; the competition to secure it was so keen that it brought a very high price, the sum covering the fine plus

the value of the glass. The excess had to be paid back to the lucky American, so that the fine did not come out of his pockets after all.

Several times in the course of his life Bunsen was injured by explosions; he was popularly believed to be minus one eye, one ear, and one lung, and there is some foundation for this, for he lost an eye when working at cacodyle, and he was slightly deaf. It was related of him that on one occasion a violent explosion threw him to the ground and made him unconscious; on coming to, his first words were: "Has any of the substance been saved?"

In 1865 Bunsen was invited to fill a chair in the University of Berlin, and after due consideration he declined the flattering call, to the delight of all educational Heidelberg. In his honour the students organised a torchlight parade; the chemists marched in a body, and carried away by enthusiasm I imprudently joined them, carrying a torch with the crowd. The procession paraded the principal streets, and then assembled in the open square before the *Aula* or central Hall of the University; there the students singing the Studenten Lieder and formed a ring, gradually closed in towards the centre, making the ring smaller, until at a given signal they threw their half-burned torches into the very centre and the pile blazed on high, making an impressive ceremonial. I have said I imprudently joined because I failed to anticipate the disagreeable consequences; the smoke of a half-a-thousand torches, the drippping grease, and the dust of the streets, combined with the moist exudation of my membranous integument, to form a black deposit that would have honoured a stoker, besides ruining a suit of clothes.

During my residence in Heidelberg a lamentable and terrible affair took place that threw a profound gloom over the University and the entire town. Two German students having quarrelled decided the earth was not large enough for both of them to live in, and resorted to the diabolical practice called the "American Duel." In a darkened room the two young men drew lots, having sworn that he who drew the black ball would commit suicide. The unhappy loser went to his room and discharged a bullet into his breast, but missed his heart and lingered for several days on his death-bed; his parents were summoned by telegraph, and besought him on their knees to disclose the name of his antagonist, but he steadfastly refused and died with the secret in his breast. The students not only excused his conduct, but praised his courage, and when his remains were taken to the railway-station to be transported to a distant city, they accompanied the funeral cortège with torches and music. The students claimed he was not a suicide, for he was killed in an honourable duel, and they maintained that his opponent was not accessory to his death because he shot himself: I had many arguments with them, and never could convince them of their extraordinary tergiversation.

The whole system of duelling at Heidelberg is an interesting feature of student life that I had good opportunities of observing without taking part, but, as Kipling says, "that is another story."

The intimacy of Bunsen and Kopp is well known; I have often seen them walk through the narrow streets hand-in-hand like affectionate school-girls, Bunsen's large frame and Kopp's diminutive stature making a strong contrast.

Bunsen had great talents and personal attractions, yet he did not succeed in fostering original work on the part of those who studied with him; I think this is partly due to the fact they were chiefly beginners, and when they had acquired the rudiments of general chemistry they took to the fertile fields of organic chemistry under other masters. Yet his pupils include some men of high rank in the profession—Lothar Meyer, Sir Henry Roscoe, Beilstein, Lieben, and Carius.

I last saw Geheimerath Bunsen during a brief visit to Heidelberg in 1891; he had retired from active duty and complained of the infirmities of advancing years, being subject to rheumatism; but he exhibited the same cordial manner, the charming smile, and a willingness to listen to the accounts of Americans who had pursued their studies in the Heidelberg Laboratory. Bunsen died after a lingering illness, August 16th, 1899, at the great age of 88.

Of the charm of residence in the picturesque little city on the Neckar, with its magnificent ruined castle, its attractive forest-covered hills threaded by enticing paths, its historical associations, and its excellent beer, there can be but one opinion; but in winter we often felt the truth of the old couplet:—

"Heidelberg ist eine schöne Stadt
Wenn es ausgeregnet hat!"

SEPARATION OF IRON FROM CHROMIUM, ZIRCONIUM, AND BERYLLIUM BY THE ACTION OF GASEOUS HYDROCHLORIC ACID ON THE OXIDES.*

By FRANKE STUART HAVENS and ARTHUR FITCH WAY.

It has been shown in a former paper from this laboratory (Gooch and Havens, *Am. Journ. Sci.*, vol. viii., No. 41, May, 1899; Chemical News, vol. lxxx., p. 39) that iron oxide may be completely volatilised as chloride by a strong current of hydrochloric acid gas acting at a temperature of 450—500°, and also that the addition of a little free chlorine to the gaseous hydrochloric acid renders this action complete at lower temperatures (180—200°) without the danger of error arising from the liability of ferric chloride to dissociation, or from deficiency of oxidation in the oxide treated, or mechanical loss due to too rapid volatilisation. It has also been shown that this reaction can be employed for the separation of iron and aluminum, taken as the oxides, and its application to the separation of iron from other metallic oxides has been suggested.

The oxides of chromium, zirconium, and beryllium, like aluminum oxide, are not acted upon by a current of dry hydrochloric acid gas at the temperatures before mentioned, and these oxides also can be entirely freed from iron by this reaction, as the experiments to be described will show. The procedure was the same in each case and analogous to that employed for the separation of iron from aluminum. A mixture of a weighed portion of one of these oxides with a weighed portion of ferric oxide, contained in a porcelain boat and placed within a roomy glass tube supported in a small combustion furnace, was submitted to the action of a dry current of hydrochloric acid gas and chlorine generated by dropping sulphuric acid upon a mixture of strong hydrochloric acid, common salt, and a small amount of manganese dioxide. The gas was admitted at one end of the combustion tube and passed out at the other through a water trap, while the required temperature (from 200—300°) was maintained by regulating the various burners of the furnace. The time of action varies somewhat with the condition of the oxide to be volatilised, and the temperature, generally an hour's heating at 200°, proves sufficient for the complete removal of 0·1 grm. of iron. At higher temperatures the action is more rapid; but the lighter oxide, the beryllium especially, is liable to mechanical loss through the too rapid volatilisation of the iron, as Experiment 17, where a temperature of 500° was used, will show. It is better, therefore, to use lower temperatures, raising the heat for a few minutes when the action is apparently complete to ensure the removal of the last traces of iron. Tests showed the residual oxides from which the ferric oxides had been removed in this manner to be entirely free from iron.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. viii., September, 1899.

Expt.	Fe_2O_3 taken. Grm.	Cr_2O_3 taken. Grm.	Cr_2O_3 found. Grm.	Error. Grm.
1	—	0·1008	0·1008	0·0000
2	0·1007	0·1006	0·1006	0·0000
3	0·1007	0·1000	0·1002	+0·0002
4	0·1010	0·1005	0·1003	−0·0002
5	0·1019	0·1006	0·1005	−0·0001
6	0·2007	0·1003	0·0999	−0·0004
		ZrO_2 taken.	ZrO_2 found.	
7	—	0·1516	0·1516	0·0000
8	0·1053	0·1010	0·1010	0·0000
9	0·1204	0·1519	0·1523	+0·0004
10	0·1236	0·1516	0·1517	+0·0001
11	0·2150	0·1517	0·1519	+0·0002
		BeO taken.	BeO found.	
12	—	0·1309	0·1311	+0·0002
13	—	0·1285	0·1285	0·0000
14	0·0997	0·0456	0·0457	+0·0001
15	0·1045	0·1099	0·1099	0·0000
16	0·1215	0·1080	0·1081	+0·0001
17	0·1510	0·1305	0·1290	−0·0015
18	0·2030	0·1081	0·1083	+0·0002

The separation of iron from chromium, zirconium, and beryllium by this method is obviously complete within very satisfactory limits of error.

ON THE ESTIMATION OF THALLIUM AS THE CHROMATE.*

By PHILIP E. BROWNING and GEORGE P. HUTCHINS.

Crookes has shown (Chem. News, viii., 255) that the chromate precipitated by the addition of potassium dichromate to an alkaline solution of a thallous salt has the constitution of a neutral salt and is very insoluble in water—100 parts of water at 100° C. dissolving about 0·2 part, and at 60° C. about 0·03 part. He has also made use of this reaction (Chem. News, vii., 145) to effect a rough separation of thallium from cadmium.

The object of this paper is to describe some work directed toward a study of the application of this reaction to the gravimetric estimation of thallium and the best conditions under which to effect the precipitation. For the work, a solution of thallous nitrate was made by dissolving 10 grms. in water, making up to a litre. The standard was determined by taking measured and weighed portions from a burette, precipitating with a slight excess of potassium iodide, agitating to bring about a good separation of the thallous iodide, and allowing to stand until the supernatant liquid was clear. The iodide was then filtered off upon an asbestos felt contained in a perforated platinum crucible, the whole having been previously ignited and weighed, washed with a mixture of alcohol and water, dried over a low flame, and weighed to a constant weight. The filtrate, which together with the washings seldom amounted to more than 50 c.m.^{3}, was evaporated to dryness on a water-bath, a few drops of water added, and thus the small amount of thallous iodide which had been dissolved recovered. This small insoluble residue, which seldom amounted to 1 m.grm. in weight, was filtered off, washed, and weighed as previously described. Baubigny (Chem. News, lxiv., 239) has shown this method to give very satisfactory results, and the uniformity of our determinations certainly confirms his statements.

For convenience in the calculations of results to be described later, a solution of potassium dichromate of definite strength was made. Portions of the thallium solution were drawn from a burette into test-tubes of about 100 c.m.^{3} capacity, and weighed as a check on the burette reading. The solution was heated to about 70° C. to 80° C., and a few drops of ammonia or potassium carbonate solution added to distinct alkalinity. A definite amount of the potassium dichromate in solution was delivered from a burette, care being taken to have an excess, and the contents agitated to bring about a good separation of the precipitated chromate. After the precipitate had completely settled out and the solution had become cold, the chromate was filtered upon asbestos, as described above, dried over a low flame, and weighed to a constant weight. The filtrates from several determinations were evaporated to a small volume, and in one or two cases a residue amounting to a few tenths of a milligrm. was obtained, but no appreciable quantity of dissolved chromate was thus recovered. It was found that when the precipitation was made in the cold the chromate did not flock well, but remained partly in a finely-divided condition which would run through the felt and require repeated filtration. The addition of ammonium nitrate before precipitation prevented this largely, even in the cold, but the best results were obtained by warming the solution before precipitation, and using potassium carbonate rather than ammonium hydroxide. The results follow in Table I.

Table I.

	$TlNO_3$ taken. Calculated as Tl_2O. Grm.	Tl_2CrO_4 found. Calculated as Tl_2O. Grm.	Error. Calculated as Tl_2O. Grm.
1.	0·0796	0·0791	0·0005 −
2.	0·0792	0·0788	0·0004 −
3.	0·0792	0·0786	0·0006 −
4.	0·1188	0·1177	0·0011 −
5.	0·1192	0·1186	0·0006 −
6.	0·1185	0·1178	0·0007 −
7.	0·1190	0·1185	0·0005 −
8.	0·1189	0·1183	0·0006 −
9.	0·1196	0·2000	0·0004 +
10.	0·1196	0·2005	0·0009 +
11.	0·1173	0·1173	0·0000
12.	0·1171	0·1163	0·0008 −

An attempt was made to estimate the thallium volumetrically by determining the amount of chromate in the filtrate from the thallous chromate, and by difference (the potassium dichromate originally added being known) the amount combined with the thallium in the precipitate. The method used to determine the standard of the dichromate solutions and also the chromate remaining in the filtrate was described by one of us in a previous paper from this laboratory (*Am. Journ. Sci.*, 1896, vol. i., 35). According to this procedure, the filtrate from the thallous chromate containing the excess of alkali chromate was acidified with sulphuric acid, a definite amount of a solution of arsenious oxide (previously standardised) was added, and the whole was allowed to stand a few moments until the change from the yellow to the bluish green showed the complete reduction of the chromic acid. Potassium bicarbonate was added to distinct alkaline reaction, and the arsenious oxide remaining was determined by titration with standard iodine solution. The amount of the arsenious oxide oxidised is, of course, the measure of the chromate in the solution. The amount of chromate in the original solution used being known, by subtracting

Table II.

	$TlNO_3$ taken. Calculated as Tl_2O. Grm.	Tl_2CrO_4 found. Calculated as Tl_2O. Grm.	Error. Calculated as Tl_2O. Grm.
5.	0·1192	0·1198	0·0006 +
8.	0·1189	0·1205	0·0016 +
9.	0·1196	0·1180	0·0016 −
10.	0·1196	0·1192	0·0004 −
11.	0·1173	0·1182	0·0009 +
12.	0·1171	0·1190	0·0019 +

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, viii., No. 48, 1899.

the amount thus determined in the filtrate, the chromate in combination with the thallium may be readily found, and from it the thallium estimated. Filtrates from certain precipitates of which the determinations are gives in Table I. were treated in this way, and the results (indicated by corresponding numbers) follow in Table II.

The method cannot be very accurate on account of the high molecular weight of thallium oxide as compared with that of the chromic acid determined, but the results check fairly well with the gravimetric method.

MEMOIR OF THE LATE WILLIAM JOHN COCK.

William John Cock, the subject of this memoir, was born on the 8th January, 1813, near Hemel Hempstead, in Hertfordshire. His father, Mr. Thomas Cock, was a very able chemist, and was of great service to his brother-in-law, Mr. Percival Johnson, founder of the well-known firm of Johnson, Matthey, and Co., Hatton Garden, London, in the preparation of colours for china painting, &c.

In the year 1834 William John Cock entered, under indentures of apprenticeship, the business then carried on by his uncle, under the name of Johnson and Stokes, as assayer and refiner; after having thoroughly mastered the business, and being in charge of the gold refinery, he was, in 1837, taken into partnership, the business then being carried on under the style of Johnson and Cock. He very soon effected important improvements, and his arrangement of sand baths is in use at the Hatton Garden works to this day. He also made many other important alterations and improvements in gold refining, and the recovery of silver from the refining solutions; he also organised the plant for producing uranium oxide from the mineral pitchblende.

It was, however, in dealing with the minerals of the platinum group that Mr. Cock most distinguished himself, and at one time he had no equal in the knowledge of the treatment of the metals, platinum, iridium, rhodium, and palladium. His ability and resources are said to have been almost endless, and he has been known to work for days together, hardly ever speaking, from 7 a.m. to midnight, with perhaps half an hour for a meal.

He was a first rate theoretical chemist, an excellent mechanic and carpenter, there being hardly a tool he could not handle.

In 1845, owing to a temporary failure in health, he retired from the partnership, but in the year 1849, being unable to remain idle, he returned to Hatton Garden and resumed charge of the uranium oxide manufacture.

In 1852, his health again failing, he determined to go for a sea voyage to Australia, the gold fever being then at its height, but he only remained three weeks ashore, and returned to England, when in 1853 he again went back to Hatton Garden, and this time took entire charge of the platinum refinery. Here, as usual, he effected many improvements, and always conducted the forging of the platinum ingots himself; he was in fact the first to work on large ingots of 500 and 1000 ozs. instead of the old-fashioned smaller ones.

Mr. W. J. Cock left Hatton Garden for the last time in the year 1861, and after another sea voyage, this time to New Zealand, whence he returned the following year, he finally gave up work and went to live in the country. He never married, though he was a universal favourite with both old and young. He died in December, 1892, at Ashburton, at the age of 79.

Owing to his somewhat retiring habits, his wonderful ability has not become as widely known as it should have been; if he had put himself more forward he would undoubtedly have obtained honour and distinction in the scientific world, but all his ambition seemed to be to properly complete the work he had in hand. To some this life would seem uneventful, but those who knew him appreciate how much our country, with its vast metallurgical interests, owes to him.

A NEW VOLUMETRIC METHOD FOR MAGNESIUM.*

By RICHARD K. MEADE.

(Concluded from p. 276).

The next, and the method finally adopted as the one most suited to the volumetric determination of magnesium, was the one worked out by A. Williamson and described by him in the *Journal of the Society of Dyers and Colourists*, May, 1896. A description of the method is also to be found in Sutton's "Volumetric Analysis," p. 369.

It depends, like the method of Gooch and Browning, upon the reaction between arsenic acid and potassium iodide. Williamson found that where a solution of arsenic acid contained sufficient sulphuric or hydrochloric acid the arsenic is quickly reduced from the higher to the lower state of oxidation, even in the cold, according to the reaction $As_2O_5 + 4KI + 4HCl = As_2O_3 + 4KCl + 2H_2O + 2I_2$. For every molecule of arsenic acid reduced, corresponding to two atoms of magnesium, two molecules or four atoms of iodine are liberated. This latter is titrated with sodium thiosulphate, and from the amount of standard solution required the magnesium calculated.

The process followed consisted in dissolving the precipitated magnesium-ammonium arsenate in dilute hydrochloric acid, washing the filter-paper well with the acid, and—after adding potassium iodide and allowing to stand for a few minutes—titrating with standard thiosulphate. This latter corresponded, c.c. for c.c., with the iodine solution mentioned above. Below are the results:—

No.	Stock solution taken.	Equivalent to MgO.	"Hypo" required.	Equivalent to MgO.
	C.c.	Grm.	C.c.	Grm.
1	50	0·2495	49·8	0·2490
2	50	0·2495	49·9	0·2495
3	25	0·1247	25·0	0·1250
4	25	0·1247	24·9	0·1245
5	10	0·0499	9·95	0·0498
6	5	0·0249	5·0	0·0250

Determinations required only from seven to ten minutes by this method after the arsenic was in solution, and were just as accurate as those by the longer method of digestion with potassium iodide.

The attempt was next made with success to hasten the precipitation of the magnesium by violent agitation. Fifty c.c. of the stock solution were measured into a large Erlenmeyer flask, diluted to about 500 c.c., and one-third this volume of strong ammonia and 50 c.c. of a 10 per cent solution of sodium arsenate added, the flask corked up tightly and shaken violently by hand for ten minutes. After allowing the precipitate to settle, it was filtered, and the arsenic determined as described above.

No.	Stock solution taken.	Equivalent to MgO.	"Hypo" required.	Equivalent to MgO.
	C.c.	Grm.	C.c.	Grm.
1	50	0·2495	49·9	0·2495
2	50	0·2495	49·9	0·2495
3	25	0·1247	24·8	0·1240
4	15	0·0748	15·0	0·0750
5	10	0·0499	9·9	0·4950
6	5	0·0249	4·9	0·0245

The time required for the precipitation, filtration,

* Read before the Lehigh Valley Section of the American Chemical Society, May 16, 1899. From the *Journal of the American Chemical Society*, vol. xxi., No. 9, September, 1899.

washing, re-solution, and titration had now been shortened to about three-quarters of an hour.

The standard thiosulphate was titrated against standard sodium arsenate, prepared by dissolving 12·29 grms. of pure arsenious acid in nitric acid, evaporating to dryness on a water-bath, neutralising with sodium carbonate, and diluting to one litre. Each c.c. of this solution was equivalent to 0·005 grm. of magnesium oxide. The values obtained by titration of the standard thiosulphate against this solution coincided with those obtained by titration with standard iodine solution. The values obtained by titration against standard bichromate and potassium iodide did not differ materially from those obtained by titration against standard arsenate or standard iodine.

The method finally worked out is as follows:—

Pour the solution, which should not contain too great an excess of ammonium chloride or ammonium oxalate into a large Erlenmeyer flask or a gas-bottle of sufficient capacity. Add one third the volume of the solution of strong ammonia and 50 c.c. of sodium arsenate. Cork up tightly and shake vigorously for ten minutes. Allow the precipitate to settle somewhat, and wash with a mixture of three parts water and one part strong ammonia until the washings cease to react for arsenic; avoid using an excess of the washing fluid, however. Dissolve the precipitate in dilute hydrochloric acid (1 : 1), allowing the acid solution to run into the flask in which the precipitation was made, and wash the filter-paper with the dilute acid, until the washings and solution measure 75 or 100 c.c. Cool, if not already so, and add from 3 to 5 grms. of potassium iodide, free from iodate; allow the solution to stand a few minutes, and then run in the standard thiosulphate until the colour of the liberated iodine fades to a pale straw colour. Add starch, and titrate until the blue colour of the iodide of starch is discharged. If preferred, an excess of thiosulphate may be added, then starch and standard iodine until the blue colour is produced. On adding the iodide of potassium to the acid solution, a brown precipitate forms, which, however, dissolves when the thiosulphate is added.

Below are some results upon the method as given above:—

Sample.	MgO. Gravimetric.	Thiosulphate required.	MgO. Volumetric.
	Per cent.	C.c.	Per cent.
Dolomite	21·78	43·3	21·65
		43·4	21·70
Limestone	9·16	18·2	9·10
		18·2	9·10
Slag	16·42	32·6	16·30
		32·5	16·25
Cement, Portland ..	2·57	5·1	2·55
Cement, Natural.. ..	11·03	22·0	11·00
		22·2	11·10

PICTURES PRODUCED ON PHOTOGRAPHIC PLATES IN THE DARK.*

By WILLIAM JAMES RUSSELL, Ph.D., V.P.R.S.

I THINK I may fairly assume that every one in this theatre has had their photograph taken, and consequently must have some idea of the nature of the process employed. I have, therefore, only to add, with regard to what is not visible in the process of taking the picture, that the photographic plate is a piece of glass or such like body, coated on one side by an adhesive paste which is acted on by light, and acted on in a very remarkable manner. No visible change is produced, and the picture might remain latent for years, but place this acted-on plate in a solution of, say, pyrogallol, and the picture appears. The subsequent treatment of the plate with sodium hyposulphite is for another purpose, simply to prevent the continuance of the action when the plate is brought into the light. Now, what I purpose demonstrating to you to-night is that there are other ways of producing pictures on photographic plates than by acting on them by light, and that by these other means a latent picture is formed, which is rendered visible in precisely the same way as the light pictures are.

The substances which produce on a photographic plate these results so strongly resembling those produced by light, are, some of them, metallic, while others are of vegetable origin. At first it seemed very remarkable that bodies so different in character should act in the same way on the photographic plate. The following metals—magnesium, cadmium, zinc, nickel, aluminium, lead, bismuth, tin, cobalt, antimony—are all capable of acting on a photographic plate. Magnesium most strongly, antimony but feebly, and other metals can also act in the same way, but only to a very slight extent. The action in general is much slower than that of light, but under favourable conditions a picture may be produced in two or three seconds.

Zinc is nearly as active as magnesium or cadmium, and is the most convenient metal to experiment with. In its ordinary dull state it is without the power of acting on a photographic plate, but scratch it or scrape it, and it is easy to prove that the bright metal is active. I would say that all the pictures which I have to show you, by means of the lantern, are produced by the direct action of the metal, or whatever the active body may be, on the photographic plate, and that they have not been intensified or touched up in any way. This first slide is the picture given by a piece of ordinary zinc which has been rubbed with some coarse sand-paper, and you see the picture of every scratch. Here is a piece of dull zinc on which some circles have been turned. It was exposed to the photographic plate for four hours at a temperature of 55° C. In the other cases, which are on a larger scale, a zinc stencil was polished and laid upon a photographic plate, and you see where the zinc was in contact with the plate much action has occurred. In another case a bright zinc plate was used, and a Japanese stencil interposed between it and the photographic plate, and a very strong and sharp picture is the result. The time required to produce these zinc pictures varies very much with the temperature. At ordinary temperature the exposure would have to be for about two days, but if the temperature was, say, 55° C., then half to three-quarters of an hour might be sufficient. Temperatures higher than this cannot be used except for very short times, as the photographic plate would be damaged. Contact between the zinc and photographic plate is not necessary, as the action readily takes place through considerable distances. Obviously, however, as you increase the distance between object and plate, so you decrease the sharpness of the picture, as is shown by the following pictures, which were taken respectively at a distance of 1 mm. and 3 m.m. from the scratched zinc surface. The appearance of the surfaces of different metals varies, and the following slides show the surface of a plate of bismuth, a plate of lead, and one of aluminium. On the next slide are the pictures produced by similar pieces of pure nickel and cobalt, and it clearly shows how much more active in this way nickel is than cobalt. Many alloys, such as pewter, fusible metal, brass, &c., are active bodies, and in the case of brass the amount of action which occurs is determined by the amount of zinc present. Thus you will see that a brass with 30 per cent of zinc produces hardly any action on the photographic plate, but when 50 per cent of zinc is present there is a fairly dark picture, and when as much as 70 per cent is present a still darker picture is produced.

The second class of bodies which act in the same way on a photographic plate are organic substances, and belong essentially to the groups of bodies known as terpenes. In trying to stop the action of metallic zinc,

* A Lecture delivered before the Royal Institution of Great Britain, May 5, 1899.

which I thought at the time might arise from vapour given off by the metal, copal varnish was used, but in place of stopping the action it was found to increase it, and this increase of activity was traced to the turpentine contained in the varnish. In experimenting with liquids it is convenient to use small shallow circular glass vessels such as are made for bacteriological experiments, the plate resting on the top of the vessel, and the amount of liquid in the vessel determining the distance through which the action shall take place. The following slide, produced in this way, shows how dark a picture ordinary turpentine produces. All the terpenes are active bodies. Dipentine is remarkably so; in a very short time it gives a black picture, and if the action be continued, the dark picture passes away, and you then have a phenomenon corresponding to what photographers call reversal. The strong smelling bodies known as essential oils, such as oil of bergamot, oil of lavender, oil of peppermint, oil of lemons, &c., are all active bodies, and all are known to contain in varying quantities different terpenes; therefore ordinary scents are active bodies, and this is shown by the following pictures produced by Eau de Cologne, by cinnamon, by coffee, and by tea. Certain wines also act in the same way: Sauterne gives a tolerably dark picture, but brandy only a faint one. Other oils than these essential ones are also active bodies: linseed oil is especially so; olive oil is active, but not nearly as much so as linseed oil; and mineral oils, such as paraffin oil, are without action on the photographic plate.

Interesting results are obtained with bodies which contain some of these active substances; for instance, wood will give its own picture, as is shown by the following slides: the first is a section of a young spruce tree, the next a piece of ordinary deal, and the third of an old piece of mahogany. Again, the next slide you will recognise as the picture of a peacock's feather. There is much interest in these pictures of feathers, as they distinguish the brilliant interference colours from those produced by certain pigments; the beautiful blue in the eye of the peacock's feather is without action on the photographic plate. Butterflies' wings, at least some of them, will draw, as you see, their own pictures. Linseed oil, which is a constituent of all printing ink, makes it an active body, and it can, like the zinc and other active bodies, act through considerable distances. In the picture before you the ink was at a distance of one inch from the plate, and the next slide shows what a remarkably clear and dark picture ordinary printing can produce. As the composition of printing ink varies so does its activity, and here are pieces of three different newspapers which have acted under the same conditions on the same plate, and you see how different the pictures are in intensity. Printed pictures, of course, act in the same way—here is a likeness of Sir H. Tate, taken from "The Year's Art." The pictures and printing in *Punch* always print well, so does the yellow ticket for the Friday evening lectures at the Royal Institution; also the rude trade-mark on Wills's tobacco, and it is of interest because the red pigment produces a very clear picture, but the blue printing is without action on the plate.

An interesting and important peculiarity of all these actions is that it is able to pass through certain media; for instance, through a thin sheet of gelatin. Here are two plates of zinc; both have been scratched by sand-paper; one is laid directly on the photographic plate, and the other one has a sheet of gelatin, its colour is of no note, laid between it and the sensitive plate; the picture in this case is, of course, not so sharp as when no gelatin is present, but it is a good and clear likeness of the scratches.

Celluloid is also a body which allows the action to pass through it, as is seen in this picture of a piece of perforated zinc, a picture which was produced at ordinary temperatures. Gold-beaters' skin, albumen, collodion, gutta-percha, are also bodies which are transparent to the action of the zinc and the other active bodies. On the other hand, many bodies do not allow the transmission of the action through them; for instance, paraffin does not, and among common substances writing ink does not, as is easily shown by placing ordinary paper with writing on it between the active body and the photographic plate. The active body may conveniently be either a plate of zinc or a card painted with copal varnish and allowed to dry, or a dish of drying oil. The picture of an ordinarily directed envelope shows this opacity of ink well. It is a property long retained by the ink, as this picture of the direction of a letter, written in 1801, shows; also this letter of Dr. Priestley's, dated 1795; and here is also some very faded writing of 1810, which still gives a very good and clear picture. Even if the writing be on parchment, the action passes through the parchment, but not through the ink, and hence a picture is formed.

With bodies which are porous, such as most papers, for instance, the action passes gradually through the interstices, and impresses the plate with a picture of the general structure of the intervening substance. For instance, the following pictures show the structure and the water-mark of certain old and modern writing-papers. Some modern writing papers are, however, quite opaque; but usually paper allows the action to take place through it, and combining this fact with the fact of strong activity of the printing ink, the apparently confused appearance produced on obtaining a picture from paper with printing on both sides is accounted for, as the printing on the side away from the photographic plate, as well as that next to it, prints through the paper, and is, of course, reversed.

I hope I have now given you a clear idea how a picture can be produced on a photographic plate in the dark, and the general character and appearance of such pictures. I now pass on to the important question of how they are produced. Moser suggested 50 years ago that there was "dark light," which gave rise to pictures on polished metallic plates, and lately it was suggested that pictures were produced by vapour given off by the metals themselves; the explanation, however, which I have to offer you is, I think, simpler than either of these views, for I believe that the action on the photographic plate is due to the formation of a well-known chemical compound, hydrogen peroxide, which undergoing decomposition acts upon the plate and is the immediate cause of the pictures formed. The complicated changes which take place on the sensitive plate I have nothing to say about on the present occasion, but I desire to convince you, that this body, hydrogen peroxide, is the direct cause of these pictures produced in the dark. Indirect proof has to be resorted to. Water cannot be entirely excluded, for an absolutely dry photographic plate would probably be perfectly inactive, and as long as water is present peroxide of hydrogen may be there also. But what are the conditions under which these pictures are formed? Only certain metals are capable of producing them. This list of active metals which I have mentioned to you was determined solely by experiment, and when completed it was not evident what common property bound them together. Now, however, the explanation has come, for these are the very metals which most readily cause, when exposed to air and moisture, the formation of this body, peroxide of hydrogen. Schönbein showed, as long ago as 1860, that when zinc turnings were shaken up in a bottle with a little water, hydrogen peroxide was formed, and the delicate tests which we now know for this body show that all the metals I named to you not only can in the presence of moisture produce it, but that their power of doing so follows the same order as their power of acting on a photographic plate. Again, what happened with regard to the organic bodies which act on the photographic plates? I have already mentioned that in experimenting with the metals it was accidentally observed that copal varnish was an active substance producing a picture like that produced by zinc, and that the action was traced to the turpentine present; again a process very much like groping in the dark had to be carried on in order to deter-

mine which were active and which inactive organic bodies, and the result obtained was that the active substances essentially belonged to the class of bodies known to chemists as terpenes. Now a most characteristic property of this class of bodies is that in presence of moisture and air they cause the formation of hydrogen peroxide, so that whether a metal or an organic body be used to produce a picture, it is in both cases a body capable, under the circumstances, of causing the formation of hydrogen peroxide. Passing now to experimental facts, which confirm this view of the action on sensitive plates, I may at once say that every result obtained by a metal or by an organic body can be exactly imitated by using the peroxide itself. It is a body now made in considerable quantity, and sold in solution in water. Even when in a very dilute condition it is extremely active. One part of the peroxide diluted with a million parts of water is capable of giving a picture. It can, of course, be used in the glass dishes like any other liquid, but it is often convenient not to have so much water present; and then it is best to take white blotting-paper, wet it in the solution of the peroxide, and let it dry in the air. The paper remains active for about twenty-four hours; or, what is still better, take ordinary plaster of Paris, wet it with the peroxide solution, and let it set "in a mould" so as to get a slab of it. This slab increases in activity for the first day or two after making, and retains its activity for a fortnight or more. Such a slab will give a good and dark picture in three or four seconds.

To show how similar the pictures produced by the peroxide and those by zinc are, pictures of a Japanese paper stencil, which had been paraffined to make it quite opaque, have been made by both processes, and are shown with other instances in which turpentine was used in the following slides. It is also very easy to obtain good pictures with the peroxide alone of the structure of paper, &c.; see, for instance, this one of a five-pound note and these of lace. Again, the strict similarity between the action of the peroxide and that of the metals and organic bodies is further shown by the fact that its action passes through the same media as their action does; and here are good pictures formed by the action of the peroxide after passing through a sheet of these substances. How this singular transmission can be explained I have treated of elsewhere, and time does not allow of my discussing the matter to-night.

There are many ways in which the bright active zinc surface can be modified. Draw your finger across it, press your thumb upon it, and you stop its activity, as is shown by the picture it will give. Lay a printed paper on the zinc, and let the contact continue for three-quarters of an hour, at a temperature of 55°, then bring the zinc in contact with a sensitive plate, a picture of the printing is formed; but allow the contact between the zinc and printing to continue for eighteen hours at the same temperature, and the picture then given by the zinc is the reverse of the former one. Where the ink has been is now less active than the rest of the plate. Here are slides which show these positive and negative pictures. Another way of modifying the zinc surface is interesting. You have seen that the ordinary zinc surface which has been exposed to air and moisture is quite inactive, but if a bright piece of zinc be immersed in water for about twelve hours the surface is acted on; oxide of zinc is formed, showing generally a curious pattern. Now, if the plate be dried, it will be found that this oxide is strongly active, and gives a good picture of the markings on the zinc. The oxide evidently holds, feebly combined or entangled in it, a considerable quantity of the hydrogen peroxide, and it requires long drying or heating to a higher temperature to get rid of it. Also, if a zinc plate be attacked by the hydrogen peroxide, the attacked parts become more active than the bright metal. Thus place a stencil on a piece of bright zinc, and expose the plate to the action of an active plaster of Paris slab, or to active blotting-paper for a short time, then, on removing the stencil, the zinc plate will give a very good picture of the stencil. Any inactive body—for instance, a piece of Bristol board or any ordinary soft paper—can be made active by exposing it above a solution of peroxide, or, more slowly, by exposing it to a bright zinc surface. If, for instance, a copper stencil be laid on a piece of Bristol board, and a slab of active plaster of Paris be placed on the stencil for a short time, the Bristol board will even, after it has been removed from the stencil for some time, give a good picture of the stencil. Drying oil and other organic bodies may be used in the same way to change the paper. A curious case of this occurred in printing a coloured advertisement cut out of a magazine, for there appeared printing in the picture which was not in the original. This printing was traced to an advertisement on the opposite page, which had been in contact with the one which was used; thus this ghostly effect was produced.

I believe, then, that it is this active body, hydrogen peroxide, which enables us to produce pictures on a photographic plate in the dark. There are many other curious and interesting effects which it can produce, and which I should like to have shown you, had time permitted.

I would only add that this investigation has been carried on in the Davy-Faraday Laboratory of this Institution.

Radio-active Effect of Barium Salts and Polonium.—In the course of a paper on these subjects, F. Giesel (*Wied. Ann.*, No. 9, 1899, p. 91), the author, states that a surprising difference exists in regard to the penetrating power of the rays of radium and those of polonium. While the rays from radium penetrate fairly well a silver thaler, the rays from polonium, although more intense, are absorbed by thinner metallic plates. The shadow of the hand and of metallic objects thrown by the polonium rays on a fluorescent screen are stronger in contrast than when produced by the radium rays.—*American Journal of Science*, viii., No. 48.

Magnetising Constants of Inorganic Substances.—Stefan Meyer (*Wied. Ann.*, No. 9, 1899, p. 236) has made an extended study of the behaviour of a large number of inorganic substances in the magnetic field, and gives tabulated results. One of the most interesting facts he states is in regard to erbium. In the combination Er_2O_3 it is four times stronger than Fe_2O_3. If in the pure metallic state it were as magnetic as it is in the state of oxide, one could reduce the weight of dynamos one-sixth and still obtain the same output as when iron is employed.—*American Journal of Science*, viii., No. 48.

Dispersion of the Cathode Rays by Magnetic Force.—M. Birkeland (*Phil. Mag.*, Nov., 1899, p. 478) has observed that when a narrow beam of cathode rays produced by an induction coil is deflected by a magnetic field, that certain rays are deflected more than others, and he has given to this effect the name of the magnetic spectrum. R. J. Strutt, of Trinity College, Cambridge, has examined this subject, and by the use of a storage battery of 800 cells shows that the formation of the magnetic spectrum is due to a peculiarity of the induction coil. The cathode rays produced by a battery are homogeneous.—*American Journal of Science*, vol. viii. No. 48, 1899.

Lavoisier's Monument.—At the last meeting of the Paris Academy of Sciences, M. Berthelot gave some details regarding the monument to Lavoisier, which is to be unveiled while the Paris Exhibition is open. M. Berthelot announced that a sum of 98,000 francs (nearly £4000) has been received in subscriptions, and the well-known sculptor Barrias has been entrusted with the work. The open space behind the Madeleine Church is the site selected.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, December 8th, 1899.

Prof. G. Carey Foster, F.R.S., Vice-President, in the Chair.

By the invitation of Prof. S. P. Thompson, this meeting was held in the Physical Laboratory of the City and Guilds' Technical College, Finsbury.

Prof. S. P. Thompson read a paper "*On Obliquely-crossed Cylindrical Lenses.*"

Any two cylindrical lenses crossed obliquely are optically equivalent to two other cylindrical lenses crossed rectangularly, and hence to a sphero-cylindrical lens. Owing to the difficulty of manufacturing cylindrical lenses with the axes of the opposite faces in different directions it becomes of importance to the optician to be able to calculate the constants of the equivalent, but more easily ground, sphero-cylindrical lens. To a first approximation a surface of radius of curvature "r" will impress upon a plane wave a curvature of $\frac{\mu-1}{r}$ where "μ" is the refractive index of the material. If we suppose an equi-convex cylindrical lens cut by two planes at right angles, the line of intersection of the planes passing normally through the centre of the lens, then the sections of the lens will in general be portions of ellipses. It is possible, therefore, to write down in terms of the angle which one of these planes makes with the axis the convergivity which would be impressed by the lens upon plane waves travelling in these planes. The effect of a second lens crossing the first obliquely can also be written down with respect to the same two planes. The joint effect of the two lenses can then be resolved along any two lines at right angles. Differentiating the expressions for these effects and equating to zero, we get the directions of maximum and minimum cylindricity. These directions are at right angles and represent two lenses crossed rectangularly, which are the optical equivalent of the original pair considered. The sphero-cylindrical lens is then easily obtained. From the mathematical expressions Prof. Thompson has deduced a graphical solution of the problem. The author exhibited a convenient combination of two cylindrical lenses for giving varying degrees of cylindricity. Let two lenses be ground, each being a mixed equi-cylinder consisting of a concave and convex ground at right angles to one another on the opposite faces of the glass. Two such mixed cylinders, if rotated with equal motion in opposite directions, will give a varying cylindricity of fixed direction in space. With the axis of positive cylindricity coincident they give the maximum, but when each is rotated 45° their resultant is zero. When rotated beyond 45° the resultant axis of cylindricity is negative in the fixed direction in which it was formerly positive.

Mr. T. H. Blakesley read a paper on "*Exact Formulæ for Lenses.*"

In this paper the author makes use of the definition of focal length with respect to magnifying power which he has described in the *Proceedings of the Physical Society* for November, 1897. By this method the focal length of a lens combination is simply a line, and not the distance between two definite points. Following the methods of his previous paper, Mr. Blakesley showed how it was possible to determine accurately the constants of lens combinations, and pointed out practical applications to the racking of telescopes for camera work, the determination of refractive indices of liquids, &c.

Prof. W. E. Dalby exhibited a Friction Dynamometer. The torque to be measured produces a twist in a spiral spring, and the object is to determine the amount of this twist. Side by side upon the shaft are two pulleys, one keyed to the shaft, and the other fastened to the end of the spring. The lead of one pulley upon the other therefore measures the twist. Two other pulleys are mounted upon a slide, and are joined up to the first ones by means of a continuous band similar to a Weston's differential pulley block. When the shaft is at rest the two pulleys on the slide are touching, but any motion of the shaft produces a twist in the spring, and therefore a lead of one of the shaft pulleys on the other. This produces a separation of the slide pulleys which is proportional to the lead, and therefore to the torque, and so, from a knowledge of the constants of the dynamometer and its number of revolutions per second, the power transmitted is at once determined.

Prof. S. P. Thompson read a note "*On an Organic Compound of great Double Refraction.*"

This substance is crystallised naphthalene, and it is 60 per cent more doubly refracting than Iceland spar. It is exceedingly brittle, and therefore difficult to work into prisms. Any worked surface must be at once covered with glass to prevent sublimation.

The Society then adjourned until January 26th, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 21, November 20, 1899.

Action of Hydrofluoric Acid and Fluorine on Glass.—Henri Moissan.—In order to examine the action of hydrofluoric acid on glass, the author first decomposes dry fluorides by means of sulphuric acid. The hydrofluoric acid gas is rapidly produced, and remains gaseous at a temperature of +20°, when the glass is immediately attacked. When Nordhausen sulphuric acid is used in the preparation of the acid, still the glass is attacked. Further experiments were also tried, but in all cases it was found that gaseous hydrofluoric acid attacks glass at ordinary temperatures, however carefully it was dried. Fluorine gas, obtained in a state of purity by freezing out the HF contained in it at a temperature of −92° and purifying it in every possible way, when placed in little glass bulbs and maintained at a temperature of 100° for some hours, does not attack the glass at all; but if a trace of moisture or a minute particle of organic matter is present, hydrofluoric acid is formed, and the glass attacked.

Chemical Effects produced by Becquerel Rays.—P. and Mdme. Curie.—The rays emitted by radiferous salts of barium are very active, and are capable of transforming oxygen into ozone. The radiferous products necessary for the production of ozone are all very active and very luminous. The phenomenon appears to be more directly connected with radio-activity than with luminosity. It is found that very luminous radium carbonate produces less ozone than radium chloride, which is much less luminous, but more strongly radio-active. Again, if a radium salt is contained in a glass vessel, a violet colouration is seen in the glass, which proceeds from the interior to the exterior surface. At the end of ten days or so, the bottom of the flask is almost black. With a less active product, the tint is less deep and requires a longer time to produce. This phenomenon is not due to the reduction of lead, as it occurs in glass containing no lead. The effect of Becquerel rays on platinocyanide of barium is also a chemical effect. All these phenomena point to the fact that the rays emitted by radium represent a continual development of energy.

Reciprocal Displacement of Metals.—Alb. Colson.—The employment of Crookes's vacuum, and so the elimination of the perturbing influence of atmospheric oxygen and gases retained by solid bodies, enabled the author to establish the fact that the direct displacement of silver by mercury is, in certain cases, a reversible reaction limited by a tension of metallic vapour, as a heterogeneous dissociation is by a gaseous tension. Finally, this method of working shows that sulphide and oxide of cadmium are dissociable below 600°, and this fact is shown by the transparence of cadmium.

Action of Nitric Oxide on Chromic Dichlorhydrine.—V. Thomas.—When a current of nitrogen dioxide is passed into chlorochromic acid, a very vigorous action takes place. Large quantities of yellow coloured vapour are evolved, the temperature rises rapidly, and a black mass is formed, viscous for some time, and which is difficult to transform into a homogeneous solid product, even after the prolonged action of nitric oxide. After considerable trouble, the author obtained a brown powder acting readily on water, colouring it black. Analysis shows the formula $Cr_5Cl_5O_7.2NO_2$ to express almost exactly the results of analysis :—Cr (total), 40·53 ; Cr (in state of chromic acid), 16·20 ; Cl, 27·66 ; N, 4·36. The substance is amorphous, and, on account of its easy decomposition, it is very difficult to purify. The author is continuing his researches on this substance.

Methylene Sulphate, or Sulphuric Methylal.—Marcel Delépine.—Under the name of methylene sulphate or sulphuric methylal, the author proposes to designate a neutral crystalline product, $CH_2<^{O}_{O}>SO_2$ or $CH_2O.SO_3$, which he obtained by the union of equal molecular proportions of formic aldehyde and sulphuric anhydride. By reason of its neutrality, it is considered as neutral sulphuric ether of hypothetical methylenic glycol, $CH_2<^{OH}_{OH}$, of which are known the simple ethers CH_2Cl_2, CH_2Br_2, CH_2I_2, diacetic ether ($CH_2(O.CO.CH_3)_2$), oxalic ether ($CH_2<^{O}_{O}>C_2O_2$), &c. The author describes the preparation, properties, and principal reactions of this substance.

A Method of Synthesising Parabanic Acid.—P. Cazeneuve.—Parabanic acid has been synthesised by the interaction of urea and ethyl oxalate contained in absolute alcohol in the presence of sodium ethylate. This method of formation has been contested. The author therefore proposes to produce it by reacting with oxamide and phenyl carbonate, according to the following equation :—

$$\begin{matrix} CO.NH_2 \\ | \\ CO.NH_2 \end{matrix} + CO\begin{matrix} \diagup OC_6H_5 \\ \diagdown OC_6H_5 \end{matrix} = \begin{matrix} CO.NH \\ | \\ CO.NH \end{matrix}\diagdown\!\diagup CO + 2C_6H_5.OH.$$

Analysis showed the substance prepared by this method to have the composition C = 31·40, H = 1·82, N = 24·62 ; the theoretical percentage being C = 31·58, H = 1·75, N = 24·56. It is therefore evident that the synthesis of parabanic acid has been performed.

MISCELLANEOUS

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, before Easter :—

Mr. C. Vernon Boys, Six Christmas Lectures (specially adapted for young people) on "Fluids in Motion and at Rest." Experimentally illustrated.

Professor E. Ray Lankester, Twelve Lectures on the "Structure and Classification of Fishes."

Dr. W. H. R. Rivers, Three Lectures on "The Senses of Primitive Man."

Professor H. H. Turner, Three Lectures on "Modern Astronomy."

Dr. Charles Waldstein, Three Lectures on "Recent Excavations at Argive Heræum (in Greece)."

Sir Hubert H. H. Parry, Three Lectures on "Neglected By-ways in Music."

Mr. W. L. Courtney, Three Lectures on "The Idea of Tragedy in Ancient and Modern Drama."

The Right Hon. Lord Rayleigh, Six Lectures on "Polarised Light."

The Friday Evening Meetings will begin on January 19th, when a Discourse will be given by The Right Hon. Lord Rayleigh on "Flight." Succeeding Discourses will probably be given by the Hon. C. A. Parsons, Professor J. Reynolds Green, Mr. H. Warington Smyth, Professor J. H. Poynting, Major Ronald Ross, Professor Frank Clowes, Sir Benjamin Stone, M.P., Professor J. Arthur Thomson, Sir A. Noble, Professor Dewar, and other gentlemen.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Volatilisation of Silica with Hydrofluoric Acid—Will some one kindle state why H_2SO_4 is almost invariably added when silica is estimated by volatilising with hydrofluoric acid? When bodies which form volatile fluorides like alumina are present the reason is obvious enough ; but why in the separation of silica and tungsten trioxide, say? A list indicating with what bodies sulphuric acid must be used, and why, would be particularly acceptable.—H. B.

MEETINGS FOR THE WEEK.

Wednesday, 20th.—Society of Arts, 8. "Bi-Manual Training by Blackboard Drawing," by H. Bloomfield Bare, F.R.I.B.A.

—— Microscopical, 8. "A Review of Photomicrography and its different Methods," by Edmund J. Spitta, M.R.C.S., &c.

Thursday, 21st.—Chemical, 8. "Condensation of Glycollic Aldehyde and Formation of α- and β-Acrose," by H. Jackson, B.A. "On Brasilin and Hæmatoxylin—Part III.," by A. W. Gilbody and W. H. Perkin, jun. "Action of Alcoholic Potash on Monobromoglutaric Ester," by N. E. Bowtell and W. H. Perkin, jun. "Mercurous Iodide" and "Interaction of Mercurous Nitrite and Ethyl Iodide," by P. C. Ray, D.Sc.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2091.

THE ANALYSIS OF TUNGSTEN COMPOUNDS.

By FRED IBBOTSON and HARRY BREARLEY.

In some notes on the Estimation of Tungsten (CHEM. NEWS, lxxix., 64) attention is drawn by one of us to the fact that precipitated lead tungstate may be partially decomposed by a dilute acetic acid solution and yet retain the whole of the tungsten in the precipitate. Naturally one wonders whether the acetic acid could be increased until nothing but WO_3 remained undissolved, and whether, unlike acetic, some other acid could be used to leave *all* the WO_3, and nothing else, undissolved.

On adding strong nitric acid, drop by drop, to a boiling solution of lead tunstate, a point is reached at which a change of colour, from white to yellow, takes place somewhat sharply. A few more c.c. of the acid and a little boiling developes the full yellow colour of WO_3.

This process applied to the estimation of tungsten gives surprisingly accurate results. When dilute solutions of an alkaline tungstate are being dealt with, the supernatant liquid is decanted from the precipitated lead compound through a small pulp filter, the filter placed along with the precipitate, and all treated together with the nitric acid. The following results were obtained by merely filtering off the WO_3 and igniting:—

0·1320	grm.	instead of	0·1320	grm. WO_3
0·1837	,,	,,	0·1848	,,
0·0658	,,	,,	0·0660	,,
0·0260	,,	,,	0·0264	,,

After separating from as much as 1 grm. of iron we found:—

0·1250	instead of	0·1265
0·2160	,,	0·2166
0·1665	,,	0·1670
0·1610	,,	0·1605
0·0800	,,	0·0820
0·0280	,,	0·0290

An examination of the filtrates from these precipitations showed always that an amount of WO_3 equal to 2 or 3 m.grms. was not precipitated. The accuracy of the process therefore depends on small compensatory errors.

If ammonium salts are present, the yellow colour is not developed by adding nitric acid to the precipitated lead salt; they should therefore be eliminated with caustic alkali.

A precipitate which is accurately represented by the formula $PbWO_4$ is obtained by adding lead acetate to a faintly ammoniacal solution of a tungstate containing also large quantities of ammonium nitrate (CHEM. NEWS, *loc. cit.*,), but in many cases the process is not to be recommended and is frequently impossible. The ignited, more or less acid tungstate of lead precipitated from faintly acetic acid solutions may, however, be completely dissolved in warm concentrated hydrochloric acid, and the WO_3 completely precipitated therefrom by diluting with water.

It was desirable to know the degree of interference of various elements in the estimation of tungsten according to this latter method of treatment, and by what modifications of it, if any, the presence of interfering elements could be tolerated.

The following test analyses show what effect was exercised by the presence of (I.) 1 decigrm. and (II.) 2 decigrms. of the element named. The figures are grms. of tungsten recovered, the amount added in each case being 0·1454 grm.

	I.	II.
Ammonium, Sodium, Potassium	Should be present as nitrates. Chlorides or acetates yield low results.	
Barium	0·1459	0·1459
Strontium	0·1457	—
Calcium	0·1459	0·1454
Magnesium	0·1449	0·1461
Zinc	0·1462	0·1452
Cadmium	0·4454	0·1450
Manganese	0·1448	0·1459
Nickel	0·1471	0·1455
Cobalt	0·1452	0·1460
Mercury	0·1447	0·1446
Arsenic	0·1451	0·1451
Uranium	0·1456	—
Iron	0·1467	0·1447
Silicon, Tin	Interference not avoided.	

Ba, Sr, Ca, Mg, Zn, Cd, Mn, Ni, and Co do not interfere in the least, and the WO_3 is generally quite free from any trace of them. Generally, except when the salts of the element have a characteristic colour, no indication of the presence of a foreign body is anywhere afforded.

Arsenic.—A few grms. of ammonium nitrate are added before precipitating the tungsten; any lead arsenite precipitated is disregarded, as it passes into the filtrate after treatment with HCl.

Mercury forms a precipitate with tungstates; this may also be disregarded.

Uranium forms insoluble tungstates. These cannot be disregarded, because after ignition they are not decomposed by HCl. They are soluble in a small excess of sodium carbonate, but are re-precipitated and not redissolved by a moderate excess of acetic acid. But if an excess be added *quickly*, with vigorous shaking, the solution remains clear even when boiled. The interference of uranium salts is therefore avoided as follows:—The clear solution of W and U, containing a *small* excess of soda carbonate, is heated to boiling, and 6 to 7 c.c. acetic acid, along with an excess of lead acetate, is heated simultaneously. At near the boiling-point the former solution is poured into the latter in a thin stream, with vigorous shaking. The mixed solution is just boiled, precipitate washed by decantation, &c. The WO_3 finally obtained is free from uranium.

Iron.—It is not possible to precipitate the lead tungstate and leave the iron in solution. If the iron is but partially precipitated, it is difficult to make sure that the same is not true of the tungsten also. The following process is limited by the difficulty of manipulating bulky precipitates of ferric hydrate:—

Make the mixture just alkaline, and then just acid with acetic. At this stage the tungsten is largely in combination with the iron: the portion in solution is precipitated by the addition of the lead acetate. The bulky precipitate is best washed so thoroughly by decantation that the filter is used only as a means of collecting it together. After ignition it is treated with hydrochloric acid, as though it were pure lead tungstate. Small amounts of aluminium can be similarly dealt with; chromium, however, cannot, because the ignited chromic oxide is insoluble in hydrochloric acid. As the steel-making alloys of tungsten and molybdenum are being separately dealt with, a more extended treatment of the separation of tungsten from iron, aluminium, and chromium is reserved.

Tin.—An accurate precipitation of tungsten cannot be made in the presence of tin or silicon. Tin forms compounds with tungsten which after ignition are hard, grey in colour, and not attacked by boiling hydrochloric acid Metallic tungsten powders are said to occasionally contain tin; the usual method of treatment depends on the reduc-

tion of the stannic oxide to metal on fusing the mixed oxides with potassium cyanide.

Silicon.—Bernouilli (CHEM. NEWS, v., 116) attacks insoluble tungstates by fusion with sodium carbonate. After neutralising the aqueous extract with acetic acid, he says, "The silica, if there be any, is completely separated by a slight excess of acetic acid, and may be separated by filtration." Surely some important item is missing from this description. Silica cannot be completely precipitated from the solution of an alkaline tungstate by the use of acetic acid. If it is not eliminated somehow, the tungsten cannot be precipitated completely with lead acetate. In spite of large excesses of this reagent, the presence of silicates causes part of the tungsten to pass into solution. Sometimes the filtrate is clear, sometimes opalescent; in either case it is generally possible to form a further precipitate on re-boiling. The deficiency seems to be due to the formation of silico-tungsten compounds which are not completely precipitated by lead salts. On the other hand, mercurous silico-tungstate being a very insoluble body, the whole of the tungsten may be precipitated with mercurous nitrate from a neutral solution, the silica in the ignited residue being removed by hydrofluoric acid. Mercurous nitrate seems generally to be available for the precipitation of tungsten where there is a probability of the formation of complex tungsten compounds, *e.g.*, antimonio-tungstates (Hallopeau, *Journ. Chem. Soc.*, Abs., ii., 1898, 540). Formerly silica and tungstic oxide were most frequently separated by ammonium hydrate or carbonate; material has been prepared for more than one atomic weight determination even, on the assumption that a reliable separation could be so made. Dufty, in a paper read before the Sheffield Metallurgical Society (summarised in Arnold's "Steel Works Analysis"), showed that the separation was imperfect because silica was soluble in ammonia. This observation was confirmed by Benneville, in whose previous work (*Journ. Iron and Steel Inst.*, 1895, i., 205) the separation by means of ammonia had been employed. The persistent way in which this analytical error has been perpetuated shows how comparatively rarely analytical processes are verified before adoption, and how an erroneous process may live on, or even be originated and accepted, in spite of previously published evidence invalidating it. This particular error lay in the assumption that silica was insoluble in ammonia at least after, if not before, ignition; and, so long ago as 1868, Skey (CHEMICAL NEWS, vol. xvii., p. 165) showed that both before and after ignition silica was soluble in ammonia, whilst Pibram (CHEMICAL NEWS, vol. xvii., 227) determined its solubility when variously treated.

Technical Department,
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THE RAPID EVALUATION OF METALLIC TUNGSTEN POWDERS.*

By FRED IBBOTSON and HARRY BREARLEY.

SUCH metallic tungsten powders as are used in steel-making contain over 90 per cent of tungsten, up to 4 per cent silica, about the same amount of iron, up to a few tenths per cent each of sulphur and manganese, frequently a little molybdenum, occasionally some niobium and tin, up to 3 per cent carbon, and a very variable amount of sodium tungstate and oxygen, so that an exhaustive analysis of this material is a lengthy affair.

The most important constituent is, of course, tungsten. To describe a rapid process for the estimation of this element is the chief object of this note. The estimation of the other elements is less frequently made, and there seems to be no established procedure respecting them.

The usual process for estimating the tungsten in these powders is:—Oxidise to WO_3 by heating to redness, drive off SiO_2 with HF, fuse with sodium carbonate, precipitate from neutralised solution with $HgNO_3$, and ignite to WO_3. It is usual to operate on half a grm. The only objections to be raised to this process are:—The final WO_3 is frequently contaminated with a little SiO_2; the small amount of material used makes small errors very serious; and the time absorbed from first to last is considerably greater than is desirable.

We cannot claim for the following process the theoretical accuracy of the one just outlined; we are, however, assured by experience that it gives as near an approximation to the truth as can be obtained by the longer process when applied to the comparatively pure material used in steel making; at the same time it provides other interesting and useful information.

The process is:—Weigh out 3 grms. into a counterpoised platinum dish, ignite to WO_3, and weigh (A); treat with HF and re-weigh (B). The difference $= SiO_2$. Add water and pure NaHO about half the size of a walnut; boil finally after diluting to 200—300 c.c., and filter through paper pulp; keep filtrate and washings (*a*); Ignite residue and weigh (C); dissolve in small amount of HCl (which it should do completely if properly roasted at the beginning); dilute to several times the volume, filter, ignite, and weigh the precipitated WO_3 (D); preserve the filtrate (*b*); then—

$B = WO_3 + Fe$ and Mn compounds of WO_3.

The Fe and Mn in these latter compounds are represented by C − D.

∴ B − C + D = amount of WO_3 from 3 grms. of the original powder.

The calculation—and also the usual amount of WO_3 which the iron, manganese, &c., carry along with them—may be illustrated by an actual example:—

Weighed dish	22·9400	(1)
After adding 3 grms. powder and igniting	26·5710	(2)
After HF	26·4823	(3)

(2) − (3) = 0·0887 = 3 per cent SiO_2.

Insoluble in NaHO	0·0703
WO_3 from HCl solution	0·0400
	0·0303 . . . . (4)

(3)	.. ..	26·4823
(1)	.. ..	22·9400
		3·5423
(4)	.. ..	0·0303

3·5120 WO_3 = 92·84 per cent W.

Some results obtained in the foregoing manner are here compared with the mean of two or more estimations made by precipitating with $HgNO_3$, &c.:—

Percentage W.		Other analytical items.			
Rapid process.	Precipitation with $HgNO_3$.	C.	Si.	Fe.	S.
93·70	93·86	0·87	0·51	—	—
97·70	97·54	0·05	—	—	—
96·10	96·10	0·02	—	—	—
92·80	92 94	2·46	1·40	1·00	—
95·10	95·09	1·15	0·84	0·28	—
94 50	94·49	3·41	0·24	0·42	—
93·30	93·32	0·81	0·76	0·84	—
94·90	94·81	1·54	0·51	—	—
95·00	94·90	0·65	0·52	0·53	1·28
95·50	95·20	0·43	0·93	0·38	0·22

The filtrate (*a*) and the residue (D) contain the whole of the tungsten, so that a direct estimation may be made if desired. The filtrate (*b*) contains the manganese and iron, which are separated and estimated in the usual way. The iron is not always present in the metallic state.

In our experience only sulphur has been found to affect the results. Sometimes the sulphur is almost completely evolved as H_2S on treating with dilute HCl, or as SO_2 on roasting in the muffle; in such cases it does not interfere. Sometimes, however, the sulphur is not evolved on roasting, and then the rapid process gives results too high. But as metallic tungsten loaded with sulphur, however it may exist, is not used in steel making, this source of error only rarely crops up, and is then open to very easy detection.

Although tungsten powders are not completely decomposed by aqua regia, the sulphur compounds appear to be. It is, however, nearly as expeditious to fuse with powdered potassium nitrate over a spirit-lamp, pour the dissolved melt into boiling HCl, evaporate nearly to dryness, and precipitate a fraction of the filtrate with barium chloride, &c.

Oxygen is an important constituent. Owing to the high atomic weight of tungsten, the presence of only 2 per cent of oxygen is equivalent to nearly 10 per cent of tungstic trioxide. Lower oxides of tungsten, too, are frequently indicated by the colour given to the dilute HCl when looking for sulphur. A determination of the oxygen by difference is unsatisfactory, as are all such determinations. A direct determination of the WO_3 is more or less accurately made by gently heating with *a large volume of strong* hydrochloric acid. It has been asserted that this has not the slightest action on the metallic tungsten, and it completely dissolves WO_3 *which has not been heated*. We propose to go fully into this point shortly.

Carbon may be accurately estimated by simple heating in a current of oxygen, and, if a capacious platinum boat be used, the residue may be employed for the estimation of Si, W, Fe, and Mn, as just described. Glistening spangles of what appear to be sublimed MoO_3 are frequently seen after the boat is drawn from the heated tube; these, when invisible to the naked eye, are detected on examining the broken up residue with a lens.

Ferro-tungsten may be, but it is not safe to assume that all alloys of tungsten which oxidise to a soft powder are, decarbonised by simple ignition. An alloy containing 20 per cent nickel, which yielded a soft orange pulverulent powder, was only decarbonised to the extent of 70 per cent. There is no difficulty, however, in any case in making combustions with PbO_2 or Pb_3O_4 in the same manner as for ferro-chromiums (Chemical News, vol. lxxv., p. 241).

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ON FLUORINE IN MINERAL WATERS. FLUORISED WATERS.

By CHARLES LEPIERRE.

In a recent article, M. Parmentier (*Comptes Rendus*, May 1, 1899), after having shown that the corrosion sometimes observed on glass placed in contact with certain mineral waters is due simply to an adherent deposit of silica, and not, as some people believe, to fluorine or its compounds, terminates his paper with the following words: "It has also been thought that the waters of Mont-Dore, as well as other waters, contain fluoride of calcium in solution. We have never, in the numerous analyses of mineral waters we have made, been able to detect the slightest trace of any fluorine compound whatever."

One may therefore conclude that in the mineral waters examined by M. Parmentier fluorides were not present,* or that their existence was most exceptional. To my mind this statement is much too far-reaching, and I hope I may be permitted to express my opinion on this subject, an opinion also based upon the results of a number of analyses of mineral waters.

Without here recalling the classic work of Nicklès, Gouvenain, Sainte Claire Deville, &c., on the presence of fluorides in water, I may remark that the greater number of modern chemists who have dealt with this subject have often found fluorine. M. Willin, whose authority is unquestioned in France, found it in the waters of Plombières, Bourbonne-les-Bains, &c. The same thing occurred in Germany (Fresenius, Bunsen, &c.). In Portugal the chemists who have dealt with the analysis of mineral waters have often found fluorides (Ferreira da Silva, Sousa Reis, and myself) in waters from Moledo, Cucos, Entre os Rios, Luso, &c, But, as a rule, the fluorides exist only as traces, and are nearly always imponderable. There are, however, certain waters, though rare, which are *rich in fluorides*; the most interesting example, perhaps unique in Europe, that I know of is that of the mineral water from Gerez in the north of Portugal.

These waters are much frequented, and have a truly remarkable effect in the case of maladies of the liver (from simple congestion to cirrhosis); they, however, contain only a very small proportion of mineral matter. Sousa Reis, who made the first complete analysis of this water, gives the total residue as 0·296 grm., and Le Pierre puts it at 0·310 grm. Each litre contains 22 to 25 m.grms. of an alkaline fluoride, probably that of sodium; this corresponds to 10 or 12 m.grms. of combined fluorine. Such quantities cannot be overlooked, as they represent about one-tenth of the total residue. It is sufficient to evaporate down half a litre of Gerez water in a platinum crucible to show in the most positive manner the existence of fluorides in the residue.

The analytical detection of fluorine in water may be done in four manners: 1, by the classic method (corrosion of lines drawn on glass covered with wax) by heating the residue with sulphuric acid, and closely following the instructions given by Fresenius and Nicklès; 2, if there is an excess of silica present SiF_4 can be formed, and its decomposition in the presence of water forms a very sensitive reaction; 3, by the methods of Lannes and Carnot; 4, I have often had recourse to the formation of crystals of fluosilicate of sodium, of which the small hexagonal pyramidal prisms are very characteristic (the microchemical reaction of Boricky); this last reaction is very sensitive.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 18.

* Since then (*C. R.*, June 5, 1899) M. Parmentier has remarked that he was only referring to the waters Mont-Dore and of Sainte-Honoré-les-Bains. The ambiguity, however, of the above-quoted sentence nevertheless exists.

ON THE CONCENTRATION OF SULPHURIC ACID IN IRON VESSELS.

By E. HARTMANN.

On account of the great rise in the price of platinum, the question of the concentration of sulphuric acid in vessels made of some other metal than platinum must be faced. Platinum is still employed on a very large scale, but the form of apparatus used has been greatly modified; the vessels used are much lighter than formerly, and are therefore cheaper. For some time past the author has been successfully using apparatus made of cast-iron, and we here gives some details which are certainly justified by the importance of the subject.

Acid at 54—55° B is placed in lead receivers in which it is concentrated to 61° B. It here attains a temperature of 145 to 150° C., and at this point it is run into a small cast-iron dish; it there reaches a temperature of about 180°, and a strength of 63·5—64° B. It is then run into the two actual concentrating vessels made of cast-iron, and arranged in the form of cascade. The acid from this apparatus has a strength of from 97 to 98 per cent of monohydrated sulphuric acid. The small evaporator weighs about 1200 kilos.; the two concentrators, with the domes, tubes, &c., have a weight of about 7500 kilos., so

that the whole represents a weight of about 8700 kilos. These figures apply to the apparatus giving 5500 to 6000 kilos. of acid per diem with a strength of 66° B., or 97—98 per cent of monohydrated acid. The distillate from the two principal vessels is passed, by means of two cast-iron tubes, to the refrigerators. The acid from the first has a strength of 35° B., that of the second being 60—62° B.; the latter is both clear and pure. It is again passed through the first apparatus, and acid of 66° B. strength is produced, which, though not altogether limpid, is still clear and transparent.

The small evaporator lasts about three or four months; this is certainly not a very long time, but as I shall show later on, this drawback cannot be compared with the low cost when we consider the small weight, only about 1200 kilos. The first concentrator should last six or nine months, the second a year, and even longer.

It is, of course, understood that the cast-iron must be of special quality. It should be hard, and as free as possible from all impurities. The disposition of the apparatus should also, in the author's opinion, be such that all parts should be in contact with the fire.

We should therefore require, allowing twelve months for the second concentrator:—

	Marks.
3750 kilos. of cast-iron for the first evaporator at 0·25 mark	= 937·50
7500 kilos. for the first concentrator	= 1835·00
4800 kilos. for the preliminary concentration	= 1200·00
Total	4012·50

During this time the apparatus will have given about 20,000 tons of monohydrated sulphuric at 97—98 per cent, so that one ton of acid at 66° B. requires a capital outlay in cast-iron of two marks, or say 0·20 mark per 100 kilos. We may add that the value of the old iron is not here taken into consideration.

According to Lunge, and the author's own personal experience, the loss of platinum is from 12·9 pfennigs per 100 kilos. of acid at 1·8, that is to say, commercial acid at 92—93 per cent; that is from 1 to 1·5 grms. per ton of acid at 98 per cent, which represents an actual cost of 1980 marks per kilo.; this represents an actual nett loss of 19·8 to 29·7 pfennigs. These figures show that, as far as cost goes, the use of cast-iron for the construction of apparatus for the concentration of sulphuric acid does not surpass that incurred by the use of platinum, but it is evident that the initial outlay for cast-iron is altogether negligible when compared with the cost of platinum apparatus. A complete installation capable of yielding 6000 kilos. of acid at 97—98 per cent would cost no less than 15,000 marks, while the production of an equal quantity of acid in platinum vessels necessitates the use of two Delplace boilers, which, with the refrigerators and condensers, amounts to about 50 kilos. of pure platinum, or close on 10,000 marks.

From the above it can be seen that the use of cast-iron apparatus merits serious attention on the part of manufacturers of sulphuric acid, unless they wish to produce an acid absolutely free from iron. On the other hand I would remark that the iron dissolved is readily deposited in acid at 66° B., traces only remaining in solution. Thus a sample of acid at 66° contained 95·4 per cent of H_2SO_4, and only 0·015 per cent of Fe_2O_3; another sample from the same source contained 97·1 per cent of H_2SO_4 and 0·010 per cent of Fe_2O_3.—*Chemiker Zeitung*, 1899, p. 147.

Christmas Lectures at the Royal Institution.—On Thursday afternoon next (December 28th) Mr. C. Vernon Boys, F.R.S., will deliver the first of a Course of Six Christmas Lectures, specially adapted for young people, at the Royal Institution. The subject will be "Fluids in Motion and at Rest" (experimentally illustrated). The remaining Lectures will be on December 30, and January 2, 4, 6, 9, 1900.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To the Water Examiner, Metropolis Water Act, 1871.

London, December 11th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during November was 2·52 inches, the whole of which fell in eight days before the 11th. The thirty years' average for this month is 2·42 inches; we thus get an excess of 0·1 inch, being the first excess since April; the total deficiency for the year is now reduced to 3·74 inches, or 15·8 per cent.

Our bacteriological examinations of 496 samples have given the results recorded in the following table; we have also examined 35 other samples, from special wells, standpipes, &c., making a total of 531 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	355
New River, filtered (mean of 121 samples) ..	13
Thames, unfiltered (mean of 26 samples) ..	3724
Thames-derived waters, from the clear water wells of eight Thames-derived samples (mean of 267 samples)	11
Ditto ditto .. .. highest	140
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	513
River Lea, from the East London Company's clear water well (mean of 32 samples) . ..	7

Considering the season of the year, the London water supply continues to be of exceptional purity; and what is more remarkable is that all the water companies have been able to supply water of equally good bacteriological quality. During the month of November no less than 531 samples of the London supply have been bacteriologically examined, and the results show that the Thames-derived water was substantially of identical quality with that obtained from the River Lea and the New River, although the initial microbic impurities of the unfiltered Thames water were greatly in excess of those of either of the other sources. This is a proof of the highly efficient character of the general filtration as at present in operation.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

THE OCCLUSION OF HYDROGEN BY METALLIC COBALT AND OTHER METALS.*

By GREGORY PAUL BAXTER.

In the course of the work upon the atomic weight of cobalt, described in preceding papers from this laboratory (Richards and Baxter, *Proc. Amer. Acad.*, 1897, xxxiii., 115; 1899, xxxiv., 351; 1899, xxxv., 61), it became necessary to weigh metallic cobalt, which had been reduced from the bromide and from the oxide by means of hydrogen. A few experiments were made at the time to show that the metal in question did not occlude appreciable amounts of hydrogen, but the comparison of this result, with the conflicting accounts of others, showed that the subject was worthy of further attention.

Hempel and Thiele (*Zeit. Anorg. Chem.*, xi., 93), by quantitative combustion of metal reduced from the oxide at a high temperature, obtained no water. Neumann and Streintz (*Monatsh. Chem.*, xii., 642), on the other hand, also working with material obtained from the oxide, found that their cobalt occluded in one case 150 times, in another 50 times, its volume of hydrogen. Troost and Hautefeuille (*Comptes Rendus*, lxxx., 788) determined the occluded hydrogen by heating the metal in a vacuum and measuring the gas evolved. Ingots of cobalt, after ignition in hydrogen, yielded only 0·1 their volume of occluded gas; foil obtained by electrolysis evolved 35 volumes of hydrogen, and upon heating in hydrogen was found to have taken up 24 volumes, while powdery cobalt, obtained by reduction of the oxide, evolved 100 times its volume of hydrogen. This latter preparation proved to be pyrophoric in air, even after the hydrogen had been removed. Neumann and Streintz also observed the same property in their cobalt when exposed to an atmosphere of oxygen.

Although this evidence seems contradictory at first sight, in reality much can be said on both sides. Metallic cobalt shows widely different characteristics in its behaviour toward hydrogen according to its purity and the method by which it is prepared. In some cases the present work shows it to have occluded only traces of hydrogen or none at all; in others it occluded amounts comparable with those found by Neumann and Streintz, and Troost and Hautefeuille.

In the following experiments the occluded hydrogen was determined by the method already mentioned—combustion of the metal and determination of the water formed. For this purpose the following apparatus was used:—

Three columns of beads moistened with strong sulphuric acid were followed by a tube containing phosphoric anhydride. These were connected with a combustion tube, which contained the boat with the metal under examination, and beyond the boat a coil of copper oxide. This copper oxide was prepared by igniting a roll of copper gauze in oxygen. Beyond this apparatus was a weighed phosphoric pentoxide tube, and this in turn was connected with an aspirator through an unweighed safety drying tube.

Owing to the fact that the organic matter emanating from rubber upon combustion will yield water, rubber was wholly avoided in this apparatus, with the exception of the connections necessary for making attachment to the combustion tube. All other joints were made wholly of glass.

After the introduction of the boat containing the cobalt into the combustion tube, and before the absorption bulb was attached, a slow current of air was drawn through the tube for some time, while the copper oxide was heated to dull redness. The weighed bulb was then inserted in the circuit, and the section of the tube containing the boat was heated until oxidation of the metal took place. In order to avoid removal of oxygen from the air, which should finally fill the absorption bulb, the current of air was continued until the boat had become cool.

After each analysis the phosphoric anhydride bulb, which could be closed by means of glass stop-cocks, was wiped with a damp cloth, and allowed to stand in the balance-case one-half hour. Needless to say, before the bulb was weighed the pressure inside and out was equalised by opening one of the stop-cocks. As the time between two successive weighings was never more than two hours, and usually not more than one, atmospheric conditions did not change sufficiently to necessitate weighing the bulb by substitution, so this precaution was omitted.

Several blank experiments were carried out in which the average gain in weight of the bulb per hour was 0·2 grm. In another case a tube, the volume of which was 13·0 c.c., filled with pure hydrogen at the room temperature, was inserted in the apparatus, and the water formed by the combustion of the hydrogen was collected in the bulb. The weight of the water formed in two experiments was 0·0111 grm. and 0·0107 grm., while theory required 0·0108 grm. Evidently the apparatus was effective for its purpose.

In several instances, which have already been described (*Proc. Amer. Acad.*, xxxiv., 355), pure cobalt reduced from the bromide was heated to 500° in a hard glass tube, from which the air had previously been completely exhausted by a Sprengel air-pump. In no case was a measurable quantity of gas evolved, and the cobalt did not lose in weight. Although at the time the evidence seemed sufficient to show that this cobalt did not possess the property of occluding important amounts of hydrogen when heated in this gas, a few grms. of metal reduced from the bromide were subjected to quantitative combustion. In calculating the volumes of occluded hydrogen, given under the following analyses, the specific gravity of cobalt is assumed to be 8·5, and the weight of a litre of hydrogen, at 20° and 760 m.m. pressure, to be 0·0839 grm.

I. 2·5 grms. of cobalt yielded 0·0005 grm. of water, or 2·0 volumes of hydrogen.

II. 2·5 grms. of cobalt yielded 0·0010 grm. of water, or 4·0 volumes of hydrogen.

III. 2·5 grms. of cobalt yielded 0·0004 grm. of water, or 1·6 volumes of hydrogen.

In analyses II. and III. the original cobalt was reduced and reoxidised, and it can be seen that this treatment produced no appreciable effect upon the amount of the occluded hydrogen. It was evident that cobalt reduced from the bromide does not possess the property of occluding hydrogen to an important extent.

On the other hand, cobalt reduced originally from the oxide was found to contain amounts of hydrogen varying widely with the purity and the method of preparation. Cobalt oxide, free from alkalies and silica, was obtained by dissolving electrolytic metal in the purest nitric acid, and precipitating the cobalt as hydroxide by the addition of pure re-distilled ammonia, all in platinum vessels. No attempt was made to remove other impurities, since these could not have been present in sufficient quantities to produce an appreciable effect. This oxide was reduced in hydrogen at 400°—500°, and the metal was subjected to combustion as soon as cold. The weight of cobalt given is somewhat higher than it should be, owing to the fact that it is impossible to obtain complete reduction at the temperature employed. It will be shown later that a temperature sufficiently high to produce complete reduction alters the behaviour of the metal toward hydrogen.

IV. 2·0 grms. of cobalt yielded 0·0034 grm. of water, or 19 volumes of hydrogen.

V. 6·4 grms. of cobalt yielded 0·0105 grm. of water, or 19 volumes of hydrogen.

VI. 2·9 grms. of cobalt yielded 0·0053 grm. of water, or 21 volumes of hydrogen.

* Contributions from the Chemical Laboratory of Harvard College. From the *American Chemical Journal*, Vol. xxii., No. 5, Nov., 1899. (The investigation on the atomic weight of cobalt, of which this paper formed a part, was presented to the Faculty of Arts and Sciences of Harvard University as a thesis for the degree of Ph.D. in 1899).

As has already been suggested by Richards and Cushman (*Proc. Amer. Acad.*, xxxiv., 333), the cause of this great difference in behaviour might be explained by either of two hypotheses. The sodic bromide contained in the cobaltous bromide might be the agent which prevented the occlusion in the case of metal reduced from the bromide, or the volatility of the cobaltous bromide might allow the reduced metal to be deposited in a form essentially different from that reduced from the oxide. Two simple experiments served to decide this dilemma. In the first place the same 2·5 grms. of cobalt reduced from the bromide were leached with pure water until all soluble matter had been removed. After drying and heating in hydrogen the metal was again subjected to combustion.

VII. 2·5 grms. of cobalt yielded 0·0004 grm. of water, or 1·6 volumes of hydrogen.

The first conception that the sodic bromide protected the reduced metal was evidently at fault. Furthermore, cobalt oxide that had been precipitated in the presence of much sodic chloride by means of sodic hydrate, and which consequently contained a large amount of alkaline and siliceous impurity, was reduced as usual with the intention of determining the effect of this alkali. Upon removing the boat containing the metal from the reduction tube spontaneous oxidation took place, and it was found necessary to replace the hydrogen in the reduction tube, after it was cool, by nitrogen, and to insert the tube bodily between the drying train and the combustion tube. This cobalt differed from the samples previously examined in that it did not contract or "sinter" to any extent. Whether this effect was due to the alkalis or to silica is uncertain.* One determination of the hydrogen occluded by metal treated in this way was made.

VIII. 2·0 grms. of cobalt yielded 0·0085 grm. of water, or 48 volumes of hydrogen.

Evidently the impurities did not protect the cobalt from the hydrogen; hence one is driven to accept the second solution of the dilemma, and to decide that cobalt reduced from the bromide differs in its state from that obtained from the oxide.

The experiment already described of heating in a vacuum cobalt reduced from the bromide was now repeated with metal obtained from the oxide. In every case gas was evolved during this process, as would have been expected, and the metal upon combustion proved to contain only traces of hydrogen.

IX. 2·7 grms. of cobalt yielded 0·0008 grm. of water, or 3·5 volumes of hydrogen.

X. 5·0 grms. of cobalt yielded 0·0010 grm. of water, or 2·5 volumes of hydrogen.

XI. 5·0 grms. of cobalt yielded 0·0014 grm. of water, or 3·2 volumes of hydrogen.

That no appreciable amount of hydrogen was given off at ordinary temperatures was evident from the following analyses. The cobalt was placed in a hard glass tube, which was then exhausted, while cold, with a Sprengel air-pump. After this treatment it was subjected to combustion as usual (Analyses XII. and XIII.), and the oxide remaining from the combustion was again reduced, and the metal analysed for hydrogen as soon as cold (Analyses XIV. and XV.). It can be seen that the amounts of hydrogen obtained in the two cases are essentially the same.

XII. 2·5 grms. of cobalt yielded 0·0017 grm. of water, or 7·6 volumes of hydrogen.

XIII. 2·7 grms. of cobalt yielded 0·0035 grm. of water, or 14 8 volumes of hydrogen.

XIV. 2·5 grms. of cobalt yielded 0·0019 grm. of water, or 8 6 volumes of hydrogen.

XV. 2·7 grms. of cobalt yielded 0·0029 grm. of water, or 12·3 volumes of hydrogen.

This was further shown by passing dry air first over cold freshly reduced metallic cobalt, and then over hot copper oxide. The small amount of water formed was collected in the usual way, and is entirely in agreement with the preceding results.

XVI. 2·0 grms. of cobalt yielded 0·0006 grm. of water in one hundred and fifty minutes.

Troost and Hautefeuille, however, found that cobalt which contained one hundred times its volume of hydrogen gave up a considerable part of it in a vacuum without the application of heat.

In several analyses in which cobalt was allowed to stand in hydrogen for at least twenty-four hours at the room temperature, the amount of water obtained upon combustion was considerably larger than that obtained from metal which was subjected to combustion immediately after reduction.

XVII. 2·7 grms. of cobalt yielded 0·0160 grm. of water, or 68 volumes of hydrogen.

XVIII. 2 9 grms. of cobalt yielded 0·0117 grm. of water, or 46 volumes of hydrogen.

The metal of Analysis XVIII., when analysed immediately after reduction, yielded 0·0053 grm. of water.

In order to show that this difference was not due to a change in the metal itself (owing to the process of oxidation and reduction), equal amounts of the same preparation of oxide were reduced under conditions exactly similar. One sample (Analysis XIX.) was allowed to stand in hydrogen at the room temperature for twenty-four hours; the other sample (Analysis XX.) was subjected to combustion as soon as cold.

XIX. 2·3 grms. of cobalt yielded 0·0043 grm. of water, or 21 volumes of hydrogen.

XX. 2·3 grms. of cobalt yielded 0·0022 grm. of water, or 11 volumes of hydrogen.

From this fact that long-continued standing in cold hydrogen increases the amount of gas occluded, it is evident that cobalt possesses the property of taking up hydrogen at ordinary temperatures. This occlusion progresses only slowly in the cold, however, for the amount taken up in twenty-four hours was less than that occluded during ordinary reduction and cooling. In the following cases the metal was first heated in a vacuum, and then allowed to stand in an atmosphere of hydrogen for twenty-four hours at the room temperature.

XXI. 2·7 grms. of cobalt yielded 0·0020 grm. of water, or 8·5 volumes of hydrogen.

XXII. 2·7 grms. of cobalt yielded 0·0018 grm. of water, or 7·5 volumes of hydrogen.

The same metal, after reduction and cooling in hydrogen, yielded 0·0035 grm. of water.

Cobalt reduced in hydrogen and allowed to cool in pure nitrogen occluded only traces of hydrogen.

XXIII. 1·9 grms. of cobalt yielded 0·0004 grm. of water, or 2·1 volumes of hydrogen.

XXIV. 1·9 grms. of cobalt yielded 0·0010 grm. of water, or 5·4 volumes of hydrogen.

This same cobalt, when cooled in hydrogen, yielded 0·0029 grm. of water upon combustion, or nearly 16 volumes of hydrogen.

According to Neumann and Streintz, repeated oxidation and reduction of the metal diminish its power of occluding hydrogen. From one sample they obtained first 150 volumes of hydrogen, then 50 volumes. Johnson, working with copper, noticed the same peculiarity, which is exhibited to a less striking extent by the metal used in the following two series of analyses:—

XXV. 2·7 grms. of cobalt yielded 0·0035 grm. of water, or 14·8 volumes of hydrogen.

XXVI. 2·7 grms. of cobalt yielded 0·0029 grm. of water, or 12·3 volumes of hydrogen.

XXVII. 2·7 grms. of cobalt yielded 0·0025 grm. of water, or 10·5 volumes of hydrogen.

XXVIII. 2·7 grms. of cobalt yielded 0·0035 grm. of water, or 14·8 volumes of hydrogen.

XXIX. 2·7 grms. of cobalt yielded 0·0025 grm. of water, or 10·5 volumes of hydrogen.

* Richards and Cushman found that nickel which had been "purified" in glass vessels contained enough of these two impurities to prevent its sintering when reduced in hydrogen (*Proc. Amer. Acad.*, xxxiv., 328).

XXX. 2·7 grms. of cobalt yielded 0·0018 grm. of water, or 7·5 volumes of hydrogen.

XXXI. 2·2 grms. of cobalt yielded 0·0020 grm. of water, or 10·2 volumes of hydrogen.

XXXII. 2·2 grms. of cobalt yielded 0·0012 grm. of water, or 6·2 volumes of hydrogen.

XXXIII. 2·2 grms. of cobalt yielded 0·0019 grm. of water, or 9·9 volumes of hydrogen.

XXXIV. 2·2 grms. of cobalt yielded 0·0012 grm. of water, or 6·2 volumes of hydrogen.

During the above process the metal gradually sintered together, occupying apparently much less volume than at first. If the same metal is then heated to redness in hydrogen it sinters much more still, and yields only traces of hydrogen.

XXXV. 5·5 grms. of cobalt yielded 0·0016 grm. of water, or 3·5 volumes of hydrogen.

XXXVI. 6·2 grms. of cobalt yielded 0·0004 grm. of water, or 0·7 volume of hydrogen.

XXXVII. 2·5 grms. of cobalt yielded 0·0003 grm. of water, or 1·2 volumes of hydrogen.

Even impure oxide, obtained by igniting commercial nitrate, when heated to a high temperature in hydrogen, occluded only traces of this gas.

XXXVIII. 1·8 grms. of cobalt yielded 0·0004 grm. of water, or 2·5 volumes of hydrogen.

Metal reduced from impure oxide at low temperatures is not coherent but powdery, while pure metal shows a decided tendency to cling together. Pure metal reduced at high temperatures forms a hard solid mass. This sintering can be nothing more nor less than incipient fusion (compare Richards, *Am. Chem. Journ.*, 1898, xx., 725). Where the minute particles of metal are in close contact with one another the contraction takes place very readily, while impurities keep apart the particles of metal and necessitate the application of higher temperatures to produce the same effect.

From the results of the work just described several important conclusions can be drawn. Cobalt in the form of ingots, which present a minimum amount of surface, is known to occlude almost no hydrogen. On the other hand, cobalt reduced from the oxide at a low temperature, and consequently in a very finely divided condition, offers a maximum amount of surface, and occludes relatively large amounts of hydrogen. Electrolytic foil, which, although it possesses considerable porosity, still lies between the above two modifications in relative surface, falls between them also in the amount of hydrogen retained. Neither Neumann and Streintz, nor Troost and Hautefeuille, took any precautions to purify their cobalt from alkalis or silica. Their metal, kept from sintering together by the impurities and the low reduction temperature, was in the finest state of division; consequently it proved to be pyrophoric, and to occlude maximum amounts of hydrogen, just as in Analysis VIII. of this paper. That this property of spontaneous oxidation was not due to the hydrogen, but to the large amount of surface presented to the air, is shown by the fact that the metal used by Troost and Hautefeuille was still pyrophoric after it had been heated in a vacuum. The pure metal used in the work just described sintered considerably, even at the lowest temperature at which reduction took place, and accordingly occluded much less hydrogen than the impure metal; while even approximately pure metal, when heated to a high temperature, sintered together to such an extent that a minimum surface was presented to the hydrogen, and only traces of this gas were occluded.

The first inference is perfectly clear. The volume of occluded hydrogen depends upon the amount of surface presented, which, in the case of metals reduced from the oxide, varies with the purity of the metal and the temperature of reduction.

Again, since at ordinary temperatures the occlusion of hydrogen progresses very slowly (Analyses XXII. and XXIII.), while at the temperature of reduction, 400°—500°, it amounted to an almost negligible quantity (Analyses XXIV. and XXXV.), at some intermediate temperature the occlusion must progress at a maximum rate.

Thirdly, the time during which the metal is in contact with the hydrogen is an important factor in determining the quantity of this gas taken up.

Finally, the volatility of cobaltous bromide evidently allows the metal reduced from it to be deposited in a form more compact and coherent than that reduced from the oxide, since the presence of sodic bromide was found to have no perceptible effect upon the amount of occluded gas.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 7th, 1899.

Professor Thorpe, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Alexander Hutcheon Bennett, 61, London Road, Bromley, Kent; Oscar Joseph Cole, Wivenhoe, Colchester, Essex; Thomas Cuthbert Davison, 49, Victoria Road, New Swindon, Wilts.; Harry Medforth Dawson, Yorkshire College, Leeds; Stephen M. Dixon, University, Fredericton, New Brunswick, Canada; James Foulds, 5, Murray Street, Burnley, Lancashire; Robert W. Gray, 7, Orme Court, Bayswater; Henry Jackson, Downing College, Cambridge; Thomas Goode Joyce, The Smallthorns, Stafford; William Charles Robert Kynaston, 9, Harland Road, Higher Tranmere, Birkenhead; Arthur Robert Laws, 48, Waverley Terrace, Newcastle-on-Tyne; Alan W. Cranbrook Menzies, 11, Howe Street, Edinburgh; Edgar Ford Morris, 69, Shrewsbury Street, Old Trafford, Manchester; Herbert Newall Morris, 48, Lansdowne Road, Crumpsall, Manchester; Ernest Brooks Naylor, 73, Castle Street, Bolton; James Hart-Smith, 4, Edenvale Street, Fulham; Bertram Vincent Storr, 17, York Road, Ilford, Essex; Archie Hugh Strong, Stoneleigh Villa, 63, Herne Hill Road, Camberwell, S.E.; Gustavus Athol Waterhouse, "Ellerslie," Birrell St., Waverley, N.S.W.; Leonard Philip Wilson, 123, Chadwick Road, East Dulwich, S.E.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. James William Anderson; Francis Paul Armitage; Frederick William Armstrong; Frederic Arnold Beesley, B.Sc.; Edgar Marsh Chapman; John Arthur Dewhirst; James Dick Dougall; Frank Rawlinson Dudderidge; H. F. F. Burdett Fermor; Elliott Henry Gurney; Percy Kay, Ph.D.; Henry Wulff Kinnersley; Ernest F. Stephen Lange; William Thomas Leeming, B.Sc.; Stephen Joshua Lett; Edward Watkin Lewis; William D. McCreath; Hugh Main, B.Sc.; Harry Ainley Neale; Thomas Henry Palmer; Marchant Pearson, B.A.; Bennett C. Polkinghorne, B.Sc.; Georges Ponthieu; Frank J. Pye; William Downing Raynor, B.A.; Christopher Foulis Roundell, B.A.; William Russell; Robert Hawks Walton; F. R. Leyland Wilson, M.A.; John Wilson.

Of the following papers, those marked * were read:—

*151. "*The Oxidation of certain Organic Acids in presence of Ferrous Salts.*" By Henry J. Horstman Fenton, M.A., F.R.S., and H. O. Jones, B.A., B.Sc.

The oxidation of various organic substances in presence of iron has formed the subject of a considerable number of previous communications, and the observations are now being extended in several directions. The present paper deals with results which have recently been obtained in an extensive study of the behaviour of acids of typical

constitution when oxidised by hydrogen peroxide in presence of ferrous salts.

It is shown that, under the conditions of the experiments, the following acids are unacted upon by the reagent:—Acetic, monochloracetic, oxalic, malonic, succinic, dibromosuccinic, fumaric, maleic; whereas an energetic, and generally immediate; oxidation occurs in the case of the following acids:—Formic, glycollic, lactic, β-oxybutyric, glyceric, tartronic, tartaric, malic, citric, mucic, saccharic, pyruvic, dioxytartaric, acetylene dicarboxylic, acetone dicarboxylic, pyromucic, benzoic, picric.

The oxidation products obtained are often of considerable interest, and changes can be effected which have not been accomplished by any other means. These oxidation products are being examined, and in the present communication an account is given of the progress of the investigation.

*152. "*Oxalacetic Acid.*" By Henry J. Horstman Fenton, M.A., F.R.S., and H. O. Jones, B.A., B.Sc.

By the oxidation of malic acid in presence of ferrous salts, the authors obtained a white crystalline substance having the formula $C_4H_4O_5$, which, on examination, was found to be free oxalacetic acid. The hydrazone crystallises in lustrous prisms, and, when heated with dilute sulphuric acid, gives the phenylpyrazoloncarboxylic acid which was obtained by Wislicenus and by Buchner from the ethyl and methyl esters. Further identification is afforded by the formation of the methyl ester and its hydrazone, by the colour reaction with ferric chloride, and by the formation of pyruvic acid when an aqueous solution of the acid is heated.

*153. "*Determination of the Constitution of Fatty Acids.* Part II." By Arthur William Crossley and Henry Rondel le Sueur.

In continuation of their work (*Trans.*, 1899, lxxv., 161) the authors have prepared ethylisopropylacetic acid from ethylisopropylmalonic acid, and have investigated it by their method.

Ethylisopropylmalonic acid crystallises from benzene in glistening needles melting at 131—131·5°; the *ethyl* salt is a colourless liquid boiling at 232—233°.

Ethylisopropylacetic acid, $C_2H_5{\cdot}CH(C_3H_7){\cdot}COOH$, prepared by the elimination of carbon dioxide from ethylisopropyl malonic acid, is a disagreeable smelling liquid boiling at 203°. The *ethyl* salt is a colourless liquid boiling at 164—165° (765 m.m.), and possessing a characteristic smell; the *amide* crystallises from light petroleum in silky needles melting at 134°; the *anilide* separates from light petroleum in clusters of small glistening needles melting at 114—115°; and the *paratoluidide* forms feathery needles melting at 123°.

Ethyl α-bromethylisopropylacetate is a mobile liquid boiling at 135—136° (59 m.m.), possessing a pungent smell somewhat resembling peppermint. When treated with diethylaniline, hydrogen bromide is eliminated in two ways, giving rise to a liquid having a marked odour of peppermint, and boiling at 175—180°. It consists of a mixture of *ethyl dimethylethylacrylate* and *ethyl methylisopropylacrylate*. On saponification, a mixture of the corresponding acid is obtained boiling constantly at 136° (55 m.m.).

When this mixture is oxidised, first with potassium permanganate, and then potassium dichromate, the products are, as expected, acetone, acetic, propionic, and isobutyric acids; thus proving that two unsaturated ethyl salts are formed by the action of diethylaniline on ethyl α-bromethylisopropylacetate.

Applying these results to the determination of the constitution of the original acid, having the formula $C_7H_{14}O_2$, since acetone is produced on oxidation, the group $(CH_3)_2C$: must be attached to the α-carbon atom in the unsaturated acid, the double bond being produced by elimination of a bromine atom from the α-carbon atom, and a hydrogen atom from an adjacent carbon atom, hence $(CH_3)_2C{:}C{\cdot}COOH$ represents the grouping of five of the seven carbon atoms. The two remaining carbon atoms must be attached to the α-carbon atom, and, as propionic acid was obtained, they must have been present as an ethyl group, therefore the formula of the unsaturated acid is $(CH_3)_2C{:}C(C_2H_5){\cdot}CO_2H$. and $(CH_3)_2CH{\cdot}CH(C_2H_5){\cdot}CO_2H$ that of the original fatty acid.

The presence of acetic and isobutyric acids is accounted for by the oxidation of the second unsaturated acid produced, namely, methylisopropylacrylic acid.

*154. "*The Reaction between Sulphuric Acid and Potassium Ferrocyanide.*" By R. H. Adie, M.A., B.Sc., and K. C. Browning, B.A.

The authors have made a quantitative investigation of the action of sulphuric acid of concentrations varying from that of H_2SO_4 (98 per cent) to $H_2SO_4,8H_2O$ on potassium ferrocyanide with the following results:—

The salt dissolves in acid of strengths corresponding to H_2SO_4 and H_2SO_4,H_2O, with the formation of potassium sulphate and hydroferrocyanic acid; there is only a slow and incomplete formation of carbon monoxide.

In acid of the strength represented by $H_2SO_4,2H_2O$, the decomposition of the salt results in the formation of carbon monoxide: this reaction accounts for all the cyanogen in the salt.

With more dilute acid of the composition of from $H_2SO_4,4H_2O$ to $H_2SO_4,10H_2O$, the products are hydrocyanic acid and Everitt's salt, $K_2Fe_2Cy_6$. At the latter dilution all the cyanogen in the salt appears as hydrocyanic acid, while the formation of carbon monoxide practically ceases with acid of $H_2SO_4,4H_2O$ strength.

The authors discuss the mechanism of the reaction (i.) through the formation and hydrolysis of hydroferrocyanic acid by means of the dilute sulphuric acid; (ii.) through the action of the potassium sulphate first formed on the hydroferrocyanic acid, with the intermediate formation of Everitt's salt. The latter reaction only takes place in fairly concentrated solutions, whilst the former alone occurs with acids more dilute than that represented by $H_2SO_4,10H_2O$. Other conditions influencing the reactions are also fully discussed.

*155. "*The Sulphates of Bismuth.*" By R. H. Adie, M.A., B.Sc.

The author has investigated the conditions of formation and limits of existence of the sulphates of bismuth, and has found that from sulphuric acid of any strength between those represented by $H_2SO_4,6H_2O$ and $H_2SO_4,12H_2O$, a basic bismuth sulphate having the formula $5Bi_2O_3,11SO_3,17H_2O$ crystallises out; if between $H_2SO_4,3H_2O$ and $H_2SO_4,5H_2O$, the sulphate may be represented as $Bi_2O_3,4SO_3,7H_2O$, and if the strength be between H_2SO_4,H_2O and $H_4SO_4,2H_2O$, the salt obtained has the composition $Bi_2O_3,4SO_3,3H_2O$. From sulphuric acid itself, the sulphate which crystallises out at temperatures above 170° has the formula $Bi_2O_3,4SO_3,H_2O$; if below 170°, $Bi_2O_3,4SO_3,10H_2O$.

This temperature 170° is that at which the acid sulphates are decomposed when heated in an air-bath, the normal bismuth sulphate, $Bi_2O_3,3SO_3$, being formed.

156. "*On Sulphates of the Form $R_2SO_4,2MSO_4$, especially those of Isometric Crystallisation.*" By F. R. Mallet.

During an examination of langbeinite, ($K_2SO_4,2MgSO_4$), from the Punjab (*Min. Mag.*, 1899, xii., 159), the author noticed that the mineral, which fuses at a red heat, on cooling solidifies to a more or less distinctly crystalline mass. This observation naturally suggested that the salt might probably be artificially produced by fusing potassium and magnesium sulphates together in the proper proportions. The crystalline mass obtained on cooling the fused sulphates contains especially in the cavities abundant octahedral crystals sometimes over a millimetre in diameter.

As it seemed probable that other salts of similar constitution might be produced in the same way, the author has prepared the following sulphates of isometric sym-

metry: $K_2SO_4,2MgSO_4$; $K_2SO_4,2ZnSO_4$; $K_2SO_4,2MnSO_4$; $K_2SO_4,2NiSO_4$; $K_2SO_4,2CoSO_4$; $Rb_2SO_4,2MgSO_4$.

Measurements of the angles of the crystals, and partial or complete analyses of the above salts, are given: their mode of decomposition by absorption of water is also described.

Mixed crystals of isometric symmetry containing more than two of the above metals have also been produced, as well as various anisotropic salts, which have not as yet been examined in detail.

157. "*Reactions of the so-called Dibenzylamarine.*" By Francis R. Japp, F.R.S., and James Moir, M.A., B.Sc.

In a recently published note (*Proc.*, 1899, xv., 211), the authors showed that the compound melting at 139—140°, obtained by Claus and Elbs (*Ber.*, 1880, xiii., 1420) by the action of potassium hydroxide on dibenzylamaronium chloride, and described as dibenzylamarine, is in reality benzoyl-*s*-dibenzyl-*i*-diphenylethylenediamine—

$$\begin{array}{l} C_6H_5\cdot CH\cdot N(C_7H_7)\cdot CO\cdot C_6H_5 \\ \quad\quad | \\ C_6H_5\cdot CH\cdot NH\cdot C_7H_7. \end{array}$$

The following are various experimental results obtained in the study of this substance.

Action of Nitrous Acid.—This yields, as chief product, a *nitroso*-compound, $C_{21}H_{17}(C_7H_7)_2N_2(NO)O$ (dimorphous: short needles, m. p. 166°; and oblong laminæ, (m. p. 168°), together with *dibenzylamaronium nitrate*, $C_{21}H_{17}(C_7H_7)_2N_2\cdot NO_3$, and a little lophine. The second of these three compounds was also prepared from dibenzyl amaronium chloride and silver nitrate, thus proving its constitution. When "dibenzylamarine" nitrate, $C_{21}H_{18}(C_7H_7)_2N_2O,HNO_3$, was heated at 185°, it was converted into a mixture of dibenzylamaronium nitrate and the foregoing nitroso-compound. *Dibenzylamaronium nitrite* (from the quaternary chloride and silver nitrite) is an uncrystallisable gum, quite distinct from the isomeric nitroso-compound.

Reduction with Hydriodic Acid.—By boiling "dibenzylamarine" with hydriodic acid (sp. gr. 1·7) for some hours, the following products were obtained:—As chief product, *benzoylbenzyl-i-diphenylethylenediamine*,—

$$\begin{array}{l} C_6H_5\cdot CH\cdot NH\cdot CO\cdot C_6H_5 \\ \quad\quad | \\ C_6H_5\cdot CH\cdot NH\cdot C_7H_7 \end{array}$$

(minute needles, m. p. 218°, basic, and yielding a *nitroso*-compound (m.p. 246°); *benzyl-i-diphenylethylenediamine*,—

$$\begin{array}{l} C_6H_5\cdot CH\cdot NH_2 \\ \quad\quad | \\ C_6H_5\cdot CH\cdot NH\cdot C_7H_7 \end{array}$$

(slender needles, m. p. 90°, converted by benzoic chloride into the foregoing compound melting at 218°); and, further, dibenzyl, benzylic iodide, benzoic acid, benzylamine, and ammonia.

Action of Sodium in Boiling Alcohol.—An almost quantitative yield of Grossmann's *s*-dibenzyl-*i*-diphenylethylenediamine (*Ber.*, 1889, xxii., 2301) was obtained.

Action of Potassium Hydroxide.—No action takes place in alcoholic solution at 150°, but on fusing the compound with potassium hydroxide it yielded the foregoing *s*-dibenzyl-*i*-diphenylethylenediamine, together with benzyllophine, and a crystalline non-basic substance melting at 128°, which gave figures agreeing with the formula $C_{28}H_{24}N_2O$.

Oxidation.—The authors confirmed Claus's observation that "dibenzylamarine" is not altered by boiling with chromium trioxide in glacial acetic acid solution, but found that when a little concentrated hydrochloric acid was added to the mixture, oxidation took place on boiling, and benzoylbenzyl-*i*-diphenylethylenediamine, $C_{28}H_{26}N_2O$ (m.p. 218°)—already obtained in the reduction with hydriodic acid—was formed.

Action of Heat.—The chief products were lophine and benzyllophine.

158. "*Note on Isoamarine.*" By H. Lloyd Snape, D.Sc., Ph.D.

As Japp and Moir have recently published (*Proc.*, 1899, xv., 211) their reasons for regarding the isomeride of amarine described by Brooke and the author (*Trans.*, 1899, lxxv., 208) as a racemic form of amarine, the author wishes to report that he has succeeded in separating this isomeride, by means of tartaric acid, into two varieties of equal and opposite optical activity. The author hopes to give a detailed account of these and other experiments on isoamarine at an early date.

159. "*On the Preparation of Benzene Azo orthonitrophenol.*" By J. T. Hewitt, M.A., D.Sc.

Noelting (*Ber.*, 1887, xx., 2997) has observed that the nitration of benzeneazophenol in a strong sulphuric acid solution leads to the formation of paranitrobenzene azophenol, $NO_2\cdot C_6H_4\cdot N:N\cdot C_6H_4\cdot OH$. The author of the present communication finds that by nitrating benzeneazophenol (10 grms.) with dilute nitric acid [20 c.c. nitric acid (sp. gr. 136) and 60 c.c. water] at 40°, the product of the reaction is benzene-azo-orthonitrophenol, $C_6H_5\cdot N:N\cdot C_6H_3(NO_2)(OH)$, m. p. 128·5° (corr.). This difference in behaviour can be readily explained, since Noelting nitrated a sulphate of benzeneazophenol, which is probably a derivative of quinone phenylhydrazone, $C_6H_5\cdot NH\cdot N:C_6H_4:O$, whilst the author of the present paper chose nitric acid of such a dilution as to exclude salt formation, and hence nitrated benzeneazophenol, $C_6H_5\cdot N:N\cdot C_6H_4\cdot OH$, itself. The result is not compatible with Hantzsch's formulation of the azophenols as quinonehydrazones when in the free state (*Ber.*, 1899, xxxii., 3089), since, while phenols are more readily substituted than benzene nuclei not containing hydroxyl or amino-groups, on the other hand amino-derivatives of benzene are certainly more easily substituted than quinones. Certain derivatives of benzene-azo-orthonitrophenol are described in the paper.

160. "*Some New Osazones and Tetrazones.*" By Harold A. Auden.

None of the three possible isomeric forms of tetrazine (which may be described, according to the relative positions of the ring components, as *v*-, *s*-, or *a*-tetrazines) has yet been isolated. Derivatives of the first of these are represented in the osotetrazones obtained by Pechmann by the oxidation of osazones (*Ber.*, 1888, xxi., 2751). A benzene derivative has also been obtained by Hempel (*J. Pr. Chem.*, xli., 176), and perhaps the substances named diazohydrides by Zincke (*Ber.*, 1886, xix., 1451; 1888, xxi., 543) belong to this class.

Representatives of *s*-tetrazine have been obtained by Ruhemann (*Trans.*, 1888, liii., 850; 1889, lv., 242; 1890, lvii., 50) and Pinner (*Ber.*, 1893, xxvi., 2126; 1894, xxvii., 984, 3273). Ruhemann (*Trans.*, 1899, lxxv., 1131) has obtained a dihydro-derivative of *s*-tetrazine ("tetrazoline") from monoformylhydrazine, and Pellizzari (*Atti R. Acad. Lincei*, [5], 1899, viii., 327) from diformylhydrazine.

The author has prepared certain osazones and tetrazones with a view to obtaining from them, by a process of oxidation, *v*-tetrazine,—

$$\begin{array}{l} H\cdot C:N\cdot N \\ \quad\quad \| \\ H\cdot C:N\cdot N \end{array}.$$

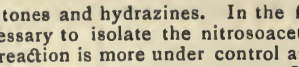
The various stages of the oxidation may probably be represented by the formulæ—

$$\begin{array}{l} CH_3\cdot C:N\cdot NC_6H_4OH \\ \quad\quad | \\ HC:N\cdot NC_6H_4OH \end{array} \rightarrow \begin{array}{l} CO_2H\cdot C:N\cdot N \\ \quad\quad\quad \| \\ H\cdot C:N\cdot N \end{array} \rightarrow \begin{array}{l} HC:N\cdot N \\ \quad\quad \| \\ HC:N\cdot N \end{array},$$

similar to those in the cases of osotriazole (*Annalen*, 1891, cclxii., 303), tetrazole (*Ber.*, 1895, xxviii., 1688), and triazole (*Ber.*, 1885, xviii., 1550, 2907).

The methods which may be used for the preparation of the substances dealt with in the paper are as follows:—1. The action of nitrosoacetone on hydrazines, with the intermediate formation of hydrazoximes. 2. The inter-

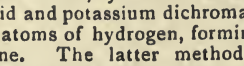
action of diketones and hydrazines. In the former case, it is not necessary to isolate the nitrosoacetone, but by so doing the reaction is more under control and the yield consequently increased by 1 to 2 per cent. In the latter method, the reaction may be thus represented by—



yielding the osazone which, by careful oxidation by means of dilute acetic acid and potassium dichromate or by amyl nitrite, loses two atoms of hydrogen, forming the corresponding tetrazone. The latter method gave better yields, the hydrazoximes frequently decomposing with the production of uninviting resinous products. In attempting to oxidise the tetrazones, further difficulties have been met with, due partly to their great stability, and partly to the difficulty in some cases of producing the tetrazone from the osazone. The actions of various oxidising agents have been studied, especially those of potassium permanganate in alkaline solution at 80—100°, and of amyl nitrite. It may here be pointed out that oxidation in acid solution is excluded because of the tendency of tetrazones to form triazole derivatives, as shown by Pechmann. A mixed osazone was also prepared, as it seemed probable that this might yield a "tetrazolium" on oxidation similar to the product obtained by Pechmann and Wedekind (*Ber.*, 1894, xxvii., 320), and that this in turn might yield further interesting products.

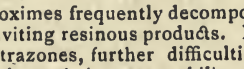
Although the experiments as yet carried out have not led to the isolation of *v*-tetrazine, the following substances have been prepared:—

Methylglyoxal-p-*ethoxyphenylhydrazoxime*,—



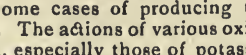
brownish yellow plates, with golden-yellow reflex, melting at 104—106°, with rapid decomposition. It can be re-crystallised from methyl alcohol, but in solution is unstable.

Methylglyoxal-p-*ethoxyphenylosazone*,—



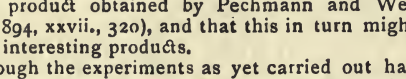
reddish yellow needles, m. p. 135. With strong sulphuric acid it gives deep green solution.

Methylglyoxal-p-*ethoxyphenylosotetrazone*,—



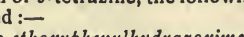
crystallises in Bordeaux-red needles, which cannot be distinguished in shade from those of methylglyoxalosotetrazone. It dissolves in strong hydrochloric acid with indigo-blue colouration, which disappears on heating; with strong sulphuric acid it gives a similar colouration, rapidly becoming green. It is not attacked by alkaline potassium permanganate in the cold, and only with difficulty at 100°.

Diazosalicylic acid,—



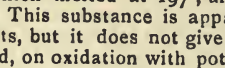
The former explodes at 155°, the latter about the same temperature, decomposition generally beginning about 10° lower. The chloride loses hydrogen chloride in the desiccator over soda and when exposed to the air. The free diazo-compound varies in shade from yellow to greenish yellow; the chloride forms nearly colourless needles. If only gently heated, both may be re-crystallised from water.

Potassium diazosalicylic acid sulphonate,—



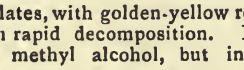
is a fairly stable compound which may be re-crystallised from water, and dried at 100°. It crystallises in yellow plates.

Hydrazine salicylic acid,—



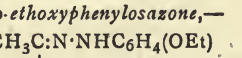
This is a slightly brown amorphous powder which melts at 148°. The hydrochloride crystallises in snowy needles which char at 150°. It reduces Fehling's solution slowly in the cold, and gives a white crystalline hydrazone with benzaldehyde.

Methylglyoxal salicylic acid osazone,—



a bright yellow crystalline powder, m. p. 192°. It gives a dark green colouration with ferric chloride. The corresponding hydrazoxime could not be isolated, and probably does not exist, as on using only one molecule of hydrazine the osazone was formed.

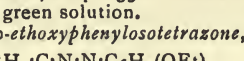
Acetyl propionyl salicylic acid osazone,—



may be obtained in very small yellow crystals by adding water to its solution in alcohol.

On boiling the crude product with alcohol, a yellow residue was invariably left; this residue melted at 220°, but yielded the same numbers on analysis as the more soluble portion which melted at 197°, and is possibly a stereoisomeride. This substance is apparently attacked by oxidising agents, but it does not give the osazone reaction. It yielded, on oxidation with potassium permanganate or potassium ferricyanide, small amounts of a white crystalline substance which gave a characteristic wine-red colouration with ferric chloride.

Methylglyoxal-methylphenyl-phenylosazone,—



yellow needles (m. p. 119—120°), slightly darker in shade than methylglyoxalphenylosazone, gives a deep red colouration with strong sulphuric acid.

The author is led to publish this preliminary note now, as, owing to a loss through fire of notes and products, some months must elapse before the results of the oxidation experiments can be published in detail.

161. "*A Series of Substituted Nitrogen Chlorides.* Part II. *The Trichloro-phenyl-acyl-nitrogen Chlorides.*" By F. D. Chattaway and K. J. P. Orton.

This paper is a continuation and completion of the authors' previous work on the substituted nitrogen chlorides which are directly obtainable from formanilide, acetanilide, and benzanilide.

It is shown that in anilides the formation of a nitrogen chloride or bromide in all cases precedes substitution in the nucleus, and that the degree of difficulty with which the transformation of these nitrogen chlorides and bromides can be effected corresponds with the relative difficulty of obtaining the transformation products directly by the action of the halogen.

The following compounds are described:—

2 : 4 : 6-*Trichloro-phenyl-formyl nitrogen chloride*, $C_6H_2Cl_3{\cdot}NCl{\cdot}CHO$, brilliant white prisms terminated by domes, m. p. 78°; 2 : 4 : 6-*trichloro-phenyl-acetyl nitrogen chloride*, $C_6H_2Cl_3{\cdot}NCl{\cdot}COCH_3$, white transparent prismatic crystals resembling cubes, m. p. 74°; 2 : 4 : 6-*trichloro-phenyl-benzoyl nitrogen chloride*, $C_6H_2Cl_3{\cdot}NCl{\cdot}COC_6H_5$, thick white prisms terminated by pyramids, m. p. 89°; *p-chloro-phenyl-benzoyl nitrogen chloride*, $C_6H_4Cl{\cdot}NCl{\cdot}COC_6H_5$, glistening short white prisms with domed ends, m. p. 79·5°.

These compounds all show the general reactions characteristic of the nitrogen halogen linkage.

162. "*The Reaction between Cupric Sulphate Solution and Magnesium, Zinc, and Iron.*" By R. M. Caven, B.Sc., F.I.C.

When magnesium, zinc, or iron reacts with cupric sulphate solution, the usual assumption of simple replacement of metal by metal is in no case found to be exactly true; cuprous oxide invariably occurs to a greater or less extent together with metallic copper in the residue.

The suggestion of Divers (*Proc.*, 1898, xiv., 57) that the cuprous oxide formed in the reaction with magnesium is due to the production of cuprous sulphate, is well in accord with the facts established; but the separation of cuprous oxide is not connected with the formation of the basic cupric sulphate produced by hydrolysis, as suggested by Divers, since it is produced in considerable quantity, together with an equivalent amount of sulphuric acid, in hot strong solutions, in which spontaneous hydrolysis of cupric sulphate with separation of insoluble basic salt does not occur. That the cuprous oxide is produced by the hydrolysis of cuprous sulphate is borne out by all the facts; and this view is supported by the observations of F. Foerster (*Zeit. Elektrochemie*, 1897, iii., 479, 493).

In all the reactions examined, with the exception of that of iron reacting with cold solutions, hydrogen is evolved, though sometimes in small quantity only. J. B. Senderens states that hydrogen is evolved in this case also (*Bull. Soc. Chim.*, 1897, [3], xvii., 271), though his statement is not confirmed by the experiments of the author.

In those cases in which only copper and cuprous oxide appeared in the residue, the hydrogen evolved was calculated from the deficiency of the acid remaining in the solution from the quantity equivalent to the cuprous oxide found. This agreed with actual measurement; and also the sum of the equivalents of the copper, cuprous oxide, and hydrogen, thus calculated, was equal to the quantity of the displacing metal employed.

The evolution of hydrogen in each case is due to one or more of the following distinct causes:—

I. Reaction of displacing metal with sulphuric acid produced—

a. By hydrolysis of cupric sulphate, resulting in separation of insoluble basic cupric salt (Divers).

b. By hydrolysis of cuprous sulphate, resulting in separation of cuprous oxide.

II. Action of the metallic couple upon the water of the solution.

III. Very slight reaction of finely-divided precipitated copper with hot dilute sulphuric acid, produced according to I.*b*.

In all cases except that of magnesium reacting with dilute solution, in which case the permanent separation of basic compounds takes place, the evolution of hydrogen may be eventually referred to the acid produced by hydrolysis of cuprous sulphate only.

The production of cuprous oxide and sulphuric acid in appreciable amount and in equivalent quantities when cupric sulphate solution is brought into contact with finely-divided copper under various conditions, shows that cuprous sulphate is produced synthetically in the above reactions. It is, however, believed that in most cases cuprous sulphate is also formed by the reduction of cupric sulphate by the replacing metal.

Camphenylone.—E. E. Blaise and G. Blanc.—The authors' experiments show that bases obtained by reducing campholenic nitrile are essentially different from dihydroaminocampholene and to the α and β aminocampholenes. Camphenylone and its derivatives do not contain the trimethylcyclopentanic radicle which exists in bodies belonging to the camphor series. The theoretical treatment of this subject appeared in a paper published in the *Bull. de la Soc. Chim. de Paris.—Comptes Rendus*, cxxix., No. 22.

NOTICES OF BOOKS.

The Metallurgy of Lead and Silver. By Henry F. Collins, Associate of the Royal School of Mines, &c. Part I. Lead. Being one of a series of Treatises on Metallurgy, written by Associates of the Royal School of Mines. Edited by Sir W. C. Roberts-Austen, K.C.B., D.C.L., F.R.S. With numerous Illustrations. London: Charles Griffin and Co., Limited. 1899. Pp. 368.

The matter contained in this volume (Part I) deals with the whole method of lead smelting. The American and German methods having been recently so thoroughly dealt with by other authors, they are only treated in a condensed manner, supplemented by information from other sources, forming a digest of the whole in a compact form.

The book is divided into three Sections and eighteen chapters. Section I. is introductory, and deals with sampling and assaying, the chemical and physical properties of lead and lead ores; these ores are for metallurgical purposes divided into two classes, viz., "sulphide ores" consisting principally of galena mixed with varying proportions of blende, pyrites, fahlerz, &c., and "oxidised ores," called in America "carbonates," which include not only cerussite, but all its mixtures with anglesite, pyromorphite, &c.

Section II. deals with the smelting of lead ores, which is practically the only method of separating lead from its ores; wet methods have been tried from time to time, but have not proved commercially successful.

The three principal methods of treatment are: 1, the *roast and reaction* method; 2, the *roast and reduction* method; and 3, the *precipitation* method. These methods are rarely employed quite independently of each other, for the residues of the first method are almost always worked up by the second or third methods, while the second method is almost always combined with the third, and often with the first as well. This Section, which forms the major part of the book, viz., 233 pages, describes all the various furnaces, hearths, and other mechanical appliances used in lead smelting, as well as in Chapter XI. examples of smelting as practised all over the world. Chapter XII. is on flue dust, its composition, collection, and treatment, and Chapter XIV. deals with the treatment of zincic sulphides. A very useful feature for facilitating reference and comparison is that details of the practice at particular localities have been as far as possible put into the form of tables; these will be found in nearly every Chapter.

Section III. is on desilverisation, in which the Pattinson and Parkes processes are both fully described and compared. The chief advantages of the Pattinson process are that it is of less complexity and requires simpler plant, and in the case of a fairly pure lead from reverberatory or hearth smelting it readily yields a lead of specially high quality. It is, however, not well suited to the treatment of impure blast-furnace lead, rich in silver, or gold-bearing. The Parkes process, on the other hand, is from 20 to 50 per cent cheaper to work; it produces a lead containing only 4 to 6 dwts. of silver against 9 to 15 dwts. by the Pattinson process; traces of gold are completely recovered, and it produces a lead for cupellation with 2000 to 5000 ozs. of silver per ton against 500 to 650 ozs. by the Pattinson process.

The Australian method of smelting and desilverisation are described in considerable detail for the first time in this volume. The ores treated are siliceous and ferruginous carbonates containing some galena, and are smelted at the Broken Hill works in fifteen 80 ton furnaces.

The whole of this valuable work is put together in an admirable manner, and may well be described as "thorough." The author, besides being an old pupil of Sir W. C. Roberts-Austen at the Royal School of Mines, has also had the benefit of his valuable assistance in editing the work; in fact, the touch of the master hand is apparent

throughout. The book is well printed and handsomely bound, its external appearance being an index of its internal excellence.

A Handbook of Physics and Chemistry. Adapted to the requirements of the First Examination of the Conjoint Examining Board of the Royal Colleges of Physicians and Surgeons, and also for general use. By Herbert E. Corbyn, B.Sc.(Lond.), and Archibald M. Stewart, B.Sc.(Lond.), Science Master of King Edward's Grammar School, Chelmsford. With 120 Illustrations. London: J. and A. Churchill.

This book is intended to aid students in the preparation for the first examination in physics and chemistry of the Royal Colleges of Physicians and Surgeons, and it is hoped that it will be useful also to those preparing for the examinations of the Pharmaceutical Society and the Royal Veterinary College. So long as the examination system remains as it is we suppose works of this kind will be necessary to aid the student to pass, but after studying the work we cannot help feeling that the man who has *passed* may have a very superficial knowledge of the sciences involved. We are glad to see that the author, in his preface, points out that "it will be necessary for the student to supplement his reading by practical work in the laboratory."

The explanations and analogies in the introduction to physics are original and good, but some of the matter in this section is decidedly poor! For instance, on page 30 there is a description of the now well-known Sprengel air-pump which, to say the least, is decidedly obsolete, and must date back quite twenty years. We scarcely expected this in an up-to-date book. Also on page 35 instructions are given for the manufacture of a mercurial thermometer which would sadly vex the most painstaking student. It is a pity that in the electrical section no description is given of the useful influence machine introduced by Mr. Wimshurst, while a whole page and a wood-cut is devoted to a very old form of plate glass friction machine.

The chemical section is by far the best part of the book, and is well and clearly written, and as complete as can be for the space devoted to it. In the list of elements we note that the name beryllium is used instead of glucinum, and that while helium is included no notice is taken of the decomposition of didymium into neodymium and praseodymium. In Appendix A will be found a choice selection of examination problems with their answers, and there is a good paragraph index.

An Elementary Course in Practical Physics. By F. Castle, M.I.M.E., Mechanical Division, Royal College of Science; Lecturer on Mechanics, Geometry, &c., Morley College, London; Author of "Notes on Advanced and Honours Theoretical Mechanics" in "The Practical Teacher." London, Edinburgh, and New York: Thomas Nelson and Sons. 1899.

This is a very valuable addition to that class of test-book which seeks to teach the student the accepted laws and principles of science, not by filling his mind with a mass of statistical information, but by causing him to make the experiments from which the laws and principles are deduced, using as far as possible apparatus prepared by himself.

To gain this end the author has spared no pains to bring together a considerable number of simple and ingenious pieces of apparatus, many quite original, with full instructions for their preparation.

A good example is found on page 154, in a method for showing the linear expansion of a metal bar by heat, consisting of two blocks of wood, a needle, and a straw! The advantages of the plentiful use of squared paper is pointed out, and the author seeks to impress upon the student the value of that neat and methodical method in working, without which success is impossible.

If anything, some of the instructions given seem almost too minute, and would seem to imply a total absence of reasoning power on part of the student; the instructions for measurement of length on page 19 is an instance, but, doubtless, the author's practical experience with modern students has shown him the need for it.

Of course, in the condensation of such a volume of technical information some errors are unavoidable. We notice one in the instructions for making an alcohol thermometer on page 163, where, after having prepared and filled the tube, the student is instructed to heat it until it is full to the top of the tube and then seal! Such a procedure is necessary where mercury is used, but alcohol thermometers need to be sealed with as much air in the tube as possible.

Examinations and problems are given to be worked out, and answers are to be found at the end of the book. There is a sensible index, and a number of good illustrations.

We consider that the book will be found of real use to both students and science masters.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 22, November 27, 1899.

Action of Dry Hydrochloric Acid on Silver and the Inverse Reaction.—M. Jouniaux.—Silver is attacked by gaseous hydrochloric acid. This fact was first noticed by Boussingault, who, by passing dry hydrochloric acid over silver heated to redness, found that silver chloride was formed, hydrogen being liberated. This experiment was confirmed by M. Berthelot, who worked at 500—550°, when the dissociation of hydrochloric acid has no influence on the progress of the phenomenon. Reciprocally, silver chloride, heated in an atmosphere of hydrogen, is reduced by this gas, there being formed metallic silver and hydrochloric acid. The author studies the effect of temperature on these two inverse reactions, experiments being conducted at 350°, 440°, and 600° for the first reaction and at 490°, 530°, and 600° for the inverse reaction.

The Colouring-matter of Digitale.—MM. Adrian and A. Trillat.—The colouring-matter in question was extracted from *Digitalis luteo* by treating the residues from the preparation of crystallised digitaline. The body obtained after numerous crystallisations consists of yellow needles melting easily at a temperature of 217—218°. The author has endeavoured to find a formula for this substance by combustion and determination of the molecular weight. The mean of two experiments gives the composition—

C	71·860
H	4·665
O	23·475 (by diff.)

which corresponds to a formula $(C_4H_3O)_n$, with molecular weight 253 The formula may therefore be taken to be $C_{16}H_{12}O_4$. This body is remarkable on account of its great stability and resistance of many chemical reagents.

MEETINGS FOR THE WEEK.

Thursday, 28th.	Royal Institution, 3. (Christmas Lectures to Young People). "On Fluids in Motion and at Rest," by Charles Vernon Boys, F.R.S. (Experimentally illustrated).
Saturday, 30th.	

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2092.

ON DOUBLE REFRACTION IN NAPHTHALENE AND A CHLORINATED DERIVATIVE.

By GREVILLE WILLIAMS, F.R.S.

IN the CHEMICAL NEWS for December 15th there is a notice of the Proceedings of the Physical Society, in which it is stated that Prof. S. P. Thompson read a note "On an Organic Compound of great Double Refraction." This substance is crystallised naphthalene, and it is said by Prof. S. P. Thompson to be 60 per cent more doubly refracting than Iceland spar. This most interesting announcement reminded me that many years ago in my article, "Naphthalene," in Watts' Dictionary of Chemistry, vol. iv., 1866, I called attention to the fact that tetra chloride of naphthalene crystallises from benzene in colourless transparent rhombohedrons, which, when deposited from half a gallon or a gallon of the solution, I had sometimes obtained nearly a quarter of an inch in length. I also say that they "exactly resemble calc-spar. They also possess powerfully the property of double refraction." I was not, however, aware that naphthalene itself was doubly refractive until I saw the notice of Prof. S. P. Thompson's discovery.

ON THE STABILITY OF GUN-COTTON AND SMOKELESS POWDERS.

By C. HOITSEMA.

THE author has already shown (*Moniteur Scientifique*, July, 1898, p. 500) that when gun-cotton is submitted to very slow heating, *in vacuo*, it gradually decomposes, leaving a black residue, and a gaseous product consisting at first of small quantities of the higher oxides of nitrogen, and finally of a simple mixture of nitrogen and binoxide of nitrogen. He has now observed that the unstable compounds contained in gun-cotton give rise to the higher oxides of nitrogen, while the stable gun-cotton gives only nitrogen and binoxide of nitrogen. From these observations the author has devised a new apparatus and method for determining the stability of gun-cotton.

The apparatus consists of two U-tubes, corked and connected with each other. In the first 1 or 2 grms. of gun-cotton are placed. The second contains glass-wool impregnated with Guttmann's reagent (diphenylamine dissolved in sulphuric acid). The tube containing the gun-cotton is then placed in an oil-bath for a quarter of an hour, at a temperature of 110° C. At the end of this time a current of carbonic acid is passed through the apparatus for a few minutes, and the blue colouration of it is observed, indicating the presence of the higher oxides of nitrogen.

The experiment is repeated in the same manner, but each time at a temperature 10° lower than the previous one, until a point is reached when the blue colour no longer appears. This temperature is noted as the index of stability.

As can be seen, the author has endeavoured to substitute an *index of temperature* for the *index of time* which has been in use up to the present. He does not approve of the test of stability proposed by Thomas (*Moniteur Scientifique*, February, 1899, p. 145) consisting of heating gun-cotton to 94—96° until red fumes appear.

Below are given the figures found for several explosives tried by the methods of Abel (at 80°), Thomas, and Hoitsema:—

Powders.	Abel. Minutes.	Thomas. Days.	Hoitsema. °C.
Gun-cotton (Stowmarket) ..	4	9—10	100
Do. (Walsrode) ..	33—39	10—10·5	100
Do. (Kruppamühle) ..	12	5	100
Powder (Muiden)	35	6—8	80
Do. (Cölln-Rottwell) ..	7—9	8—8·5	80
Ballistite (Muiden)	23—27	6·5—8 hrs.	70
Do. (Düneberg)	13	5·5—6 days	80
Cylindrical powder (Muiden)	48	5·5	90
Do. (Düneberg)	60	7—8	90

—*Zeitschrift für Angewandte Chemie*, 1899, xxx., p. 705.

THE DOUBLE AMMONIUM PHOSPHATES OF BERYLLIUM, ZINC, AND CADMIUM IN ANALYSIS.*

By MARTHA AUSTIN.

IT has been shown (*Am. Journ. Sci.*, vi., 233) that the composition of the phosphate of manganese thrown down by microcosmic salt from the solution of a pure manganous salt contains more manganese than belongs to the ideal ammonium-manganese phosphate, NH_4MnPO_4; and, further, that by acting with ammonium chloride in proper proportion the phosphate of manganese thrown down by microcosmic salt may be completely converted to the ideal ammonium-manganese phosphate. Ammonium chloride, likewise, in the case of magnesium phosphate (*Am. Journ. Sci.*, vii., 187) tends to cause the replacement of the metal by ammonia. Indeed, the replacement here is readily carried so far beyond the point corresponding to the normal ammonium-magnesium phosphate, NH_4MgPO_4, that the tendency to form a salt richer in ammonia and poorer in magnesium—perhaps something like $Mg(NH_4)_4(PO_4)_2$—must be recognised.

These facts suggested an investigation into the constitution of certain other ammonium phosphates with reference to their utility in analytical processes. Of the elements of Mendeleeff's second group, beryllium, magnesium, zinc, cadmium, and mercury are capable of yielding double ammonium phosphates, while no such compounds of calcium, strontium, and barium have been described. The solubility in ammonia of the double ammonium phosphates of the elements of the former category appears to increase as the elements of which they are compounds are removed in the series from the beryllium, and, while the same is true of the simple phosphates of members of the latter category, the extent of such solvent action is slight comparatively. According to the work recorded in the literature, calcium, barium, and strontium form individually a neutral tribasic phosphate or acid phosphates of greater or less degree of acidity, according to the conditions of precipitation. In my experience, where salts of these elements were precipitated either with ammonium phosphate or microcosmic salt in presence of varying amounts of ammonium chloride or ammonia, or both, only the recognised phosphates were obtained. The effect of ammonium salts in presence of ammonia seemed to promote the formation of the tribasic salt in the case of calcium and strontium; barium tends to form the barium acid phosphate almost exclusively, even in the presence of ammonium salts and free ammonia. No doubt ammonium phosphate of either calcium, strontium, or barium was produced under any condition. As is well known, mercury does form an ammonium-mercury phosphate, but the salt is soluble to so great a degree in ammonia, am-

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. viii., September, 1899.

monium chloride, and even in the precipitant itself, that nothing of any value for analytical work seemed likely to come from its study.

The Ammonium-beryllium Phosphate.

The ammonium-beryllium phosphate has been described by Roessler (Fresenius, *Zeit. Anal. Chemie*, 1878, 148) as a crystalline salt produced by boiling some time in ammoniacal solution the phosphate precipitated by ammonium phosphate, though the best results of this treatment failed to yield the ideal constitution of this salt, NH_4BePO_4. This same precipitate cannot be obtained, Roessler further states, by using a sodium salt as the precipitant. In order to follow out this work of Roessler, a solution of beryllium chloride for use was prepared as follows:—The pure beryllium chloride of commerce was dissolved in as little water as possible and treated for the precipitation of aluminum by ethereal hydrochloric acid (*Am. Journ. Sci.*, iv., 111). After filtering and evaporating from the filtrate the ether and a part of the hydrochloric acid, the beryllium was precipitated with ammonia, filtered to remove any members of the magnesium group, and washed free from ammonium chloride. The larger part of the precipitate was dissolved in hydrochloric acid in slight excess, and boiled with the reserved portion. After filtering, the solution was diluted to definite volume and standardised by precipitating measured portions of the solution with ammonia, filtering on asbestos under pressure in a perforated platinum crucible, igniting the residue, and weighing as the oxide. The results recorded in Section A of Table I. were obtained by precipitating definite volumes of the pure solution of beryllium chloride with ammonium phosphate in a platinum dish, dissolving the precipitate in hydrochloric acid in faint excess, and while hot precipitating slowly with dilute ammonia, boiling (while the solution was kept distinctly ammoniacal) until the flocky precipitate was entirely converted to a fine powdery, semi-crystalline, rapidly-subsiding mass. A quarter to a half hour is necessary under the most favourable conditions to cause this conversion. After cooling, the precipitate was filtered off on asbestos under pressure in a perforated platinum crucible, washed carefully with distilled water, dried, ignited, and weighed. The filtrate was tested for beryllium by boiling with ammonia. None was found in these cases, nor in any of the following work. Faint traces of chloride were found in the residues after ignition after dissolving in nitric acid and testing with silver nitrate.

The results are in every case in excess of the theory for the pyrophosphate derived by ignition of the ammonium-beryllium phosphate, possibly because the ammonium chloride present may have a tendency to form a salt too rich in ammonium (as was shown to be the case with the magnesium salt), consequently giving too much phosphoric acid in the ignited residue; or, because of inclusion of the chloride and phosphoric acid. It might reasonably be expected that some phosphoric acid may be held, since a trace of chloride was found. Either or both of these substances may have been held mechanically or in combination.

It was found that by boiling for some time the solution of beryllium chloride with microcosmic salt (6, Section B of the table), precipitating in the same manner as when ammonium phosphate was used, that the same sort of powdery mass remained as was obtained by the ammonium phosphate. The residue being tested for sodium according to the method brought out by Kreider and Breckenridge (*Am. Journ. Sci.*, ii., 263), showed sodium present to the amount of 0·0062 grm., reckoned as sodium phosphate. It may be reasonably supposed that the presence of the sodium was due to one of two causes: inclusion of the soluble phosphate, or to a tendency on the part of the beryllium to form an ammonium-sodium-beryllium phosphate (Persoz, *Liebig's Annalen*, lxv., 174; Atterberg, *Bull. Soc. Chim.*, xxiv., 358) or a sodium-beryllium phosphate (Scheffer, *Liebig's Annalen*, cix., 144), both of which are known to exist. Long boiling of the precipitates is tedious, and, unless great care is taken, may involve small losses of material; hence if the same results could be obtained with less boiling such treatment would be decidedly advantageous. The results in Section C of the table were obtained by adding microcosmic salt to the hot solutions of the chloride, boiling five minutes, cooling, filtering off on an ashless filter—because of the flocky condition of the precipitate—treating as usual before igniting the residue in a platinum crucible. The results compare well with those obtained by long boiling of the precipitated beryllium—although all are in excess of the theory. That ammonium chloride here, as in cases above, has a marked effect in changing the constitution of the phosphate precipitated by microcosmic salt is not readily seen. It is obvious that the presence of an excess of the soluble phosphate is essential to precipitate the beryllium as the double ammonium phosphate from the results recorded in Section D of the table, where, after the precipitate of beryllium phosphate had subsided and the supernatant liquid had been poured off, the precipitate dissolved in hydrochloric acid was brought down again at the boiling temperature with ammonia either alone or in presence of ammonium chloride. The results obtained show that the salt approaches the constitution of the tribasic phosphate, when it is precipitated in presence of a faint excess of phosphoric acid, even though ammonium chloride in large amount be present.

From the work described it is clear that the ammonium-beryllium phosphate is not obtained in ideal condition by precipitating a solution of the chloride with ammonium phosphate. Roessler's own results were likewise only approximately correct, as he states. It is also plain that hydrogen-sodium-ammonium phosphate precipitates the ammonium-beryllium phosphate in a condition as nearly ideal as does the ammonium phosphate, while the effect of the ammonium chloride in either case is not marked in producing a phosphate containing ammonia. Of most importance in obtaining the ammonium salt is an excess of the soluble phosphate, for when the amount of the precipitant is reduced to a little more than the theoretical amount the condition of the phosphate coincides almost exactly with the theory for the tribasic phosphate, even though a large excess of ammonium chloride be present. When there is an abundance of the precipitant the results are all in excess of the theory, which may be accounted for on the supposition that foreign material is included—the chloride of ammonia and the soluble phosphate—to a greater or less extent by the precipitate. The formation of a phosphate of beryllium containing too much ammonia and phosphoric acid, or, in case of the precipitations by microcosmic salt or sodium by the formation of a sodium-ammonium-beryllium phosphate and sodium-beryllium phosphate (known salts) is not definitely proved.

The Ammonium Zinc Phosphate.

Debray (*Comptes Rendus*, lix., 40), Bette (*Liebig's Annalen*, xv., 129), and Heintz (*Liebig's Annalen*, cxliii., 156) separately found that ammonium zinc phosphate is formed by boiling a solution of zinc sulphate with ammonium phosphate. This salt was investigated later by A. Guyard (Hugo Tamm, CHEM. NEWS, xxiv., 148), who found that if to a solution of a zinc salt of an organic or a mineral acid supersaturated with ammonia until all the zinc oxide is dissolved and made faintly acid with hydrochloric acid, sodium phosphate be added, a flocky precipitate resulted, which on being kept near the boiling point for some seconds was converted to crystalline zinc ammonium phosphate, which filtered readily, and was washed free from impurities with the greatest facility. He found that all the zinc in solution was thrown down as the ammonium zinc phosphate, which, on ignition, yielded the zinc pyrophosphate. With care in handling this process to avoid an excess of the precipitant, and the presence of sodium and potassium salts (on account of the danger of

TABLE I.

	$Be_2P_2O_7$ corresponding to $BeCl_2$. Taken. Grm.	$Be_2P_2O_7$ corresponding to $BeCl_2$. Found. Grm.	Error. Grm.	$Be_2P_2O_7$ corresponding to $BeCl_2$. Taken. Grm.	$Be_2P_2O_7$ corresponding to $BeCl_2$. Found. Grm.	Error. Grm.	$(NH_4)_2PO_4$. Grms.	NH_4Cl. Grms.
				A.				
1.	0·3578	0·3613	0·0035+				2	—
2.	0·3578	0·3808	0·0230+				2	—
3.	0·3578	0·3707	0·0129+				2	—
4.	0·3578	0·3640	0·0062+				2	—
5.	0·3578	0·3680	0·0102+				2	30
				B.			$HNaNH_4PO_4.4H_2O$.	
6.	0·3578	0·3697	0·0119+					
				C.				
7.	0·3578	0·3618	0·0040+				1·2	—
8.	0·3578	0·3680	0·0102+				1·2	—
9.	0·3578	0·3729	0·0151+				1·2	10
10.	0·3578	0·3631	0·0053+				1·2	60
				D.				
11.				0·2700	0·2589	0·0111−	0·5	—
12.				0·2700	0·2989	0·0289+	0·5	−10
13.				0·2700	0·2936	0·0236+	0·5	5—60
14.				0·2700	0·2507	0·0193−	0·5	−60

TABLE III.

	$Zn_2P_2O_7$ corresponding to $ZnSO_4$. Taken. Grm.	$Zn_2P_2O_7$ corresponding to $ZnSO_4$. Found. Grm.	Error. Grm.	Error in terms of Zinc. Grm.	$Zn_2P_2O_7$ corresponding to Zn left in the filtrate. Grm.	$(NH_4)_2PO_4$. Grm.	NH_4Cl. Grm.	Time of standing. Hours.
					A.			
1.	0·6355	0·6206	0·0149−	0·0060−	Trace	3·13	—	1½
2.	0·6355	0·6254	0·0101−	0·0040−	Trace	3·13	—	16
3.	0·6355	0·6300	0·0055−	0·0022−	Trace	3·13	—	16
					B.	$HNaNH_4PO_4.4H_2O$.		
4.	0·6355	0·6271	0·0084−	0·0034−	Trace	4·47	0·5	1
5.	0·6355	0·6256	0·0099−	0·0040−	None	4·47	0·5	20
					C.			
6.	0·6355	0·6285	0·0070−	0·0028−	None	4·47	10	½
7.	0·6355	0·6304	0·0051−	0·0020−	None	4·47	10	¾
8.	0·6355	0·6295	0·0060−	0·0024−	None	4·47	10	2½
9.	0·6355	0·6335	0·0020−	0·0008−	None	4·47	10	16
10.	0·6355	0·6381	0·0026+	0·0010+	None	4·47	20	½
11.	0·6355	0·6379	0·0024+	0·0009+	None	4·47	20	2
12.	0·6355	0·6386	0·0031+	0·0012+	None	4·47	20	½
13.	0·6355	0·6393	0·0038+	0·0014+	None	4·47	20	½
14.	0·6367	0·6355	0·0012+	0·0005+	None	4·47	30	16
					D.			
15.	0·6355	0·6172	0·0183−	0·0072−	0·0108	0·894	20	3
16.	0·6355	I. 0·6227 II. 0·0040	0·0098−	0·0039−	None	I. 0·894 II. 3·576	20	¼
					E.			
17.	0·6355	0·6270	0·0085−	0·0034−	None	4·47	—	3
18.	0·6355	0·6125	0·0230−	0·0093−	0·0148	4·47	—	18
19.	0·6355	0·6303	0·0052−	0·0021−	0·0020	4·47	10	18

TABLE IV.

	$Cd_2P_2O_7$ corresponding to $CdCl_2$. Taken. Grm.	$Cd_2P_2O_7$ corresponding to $CdCl_2$. Found. Grm.	Error. Grm.	Error in terms of cadmium. Grm.	$Cd_2P_2O_7$ corresponding to Cd found in the filtrate. Grm.	$HNaNH_4PO_4.4H_2O$. Grms.	NH_4Cl. Grm.	Time of standing. Hours.
1.	0·6972	0·6201	0·0771−	0·0434−	0·0059	4·5	—	3
2.	0·6972	0·6135	0·0837−	0·0471−	None	4·5	—	16
3.	0·6972	0·6134	0·0838−	0·0471−	None	4·5	—	16
4.	0·6972	0·6792	0·0180−	0·0101−	Trace	4·5	1	16
5.	0·6972	0·6831	0·0141−	0·0079−	0·0113	4·5	10	2
6.	0·6972	0·6976	0·0004+	0·0002+	Trace	4·5	10	16
7.	0·6972	0·6969	0·0003−	0·0002−	Trace	4·5	10	18
8.	0·6972	0·6962	0·0010−	0·0006−	Trace	4·5	10	16
9.	0·6972	0·6891	0·0081−	0·0045−	0·0191	4·5	20	16
10.	0·6972	0·6972	0·0000	0·0000	Trace	4·5	20	16
11.	0·6972	0·6942	0·0030−	0·0016−	Trace	4·5	20	16
12.	0·6972	0·6737	0·0235−	0·0132−	0·0304	4·5	30	16
13.	0·6972	0·5655	0·1317−	0·0741−	0·1378	4·5	30	16
14.	0·6972	0·6922	0·0050−	0·0023−	0·0088	4·5	10	16
15.	0·6972	0·3209	0·3763−	0·2117−	0·2449	4·5	—	16

occlusion), the precipitation of the ammonium zinc phosphate, ignition, and weighing as the pyrophosphate made, Guyard believed, an ideal process for the estimation of zinc. Although there was slight solubility of the salt, it made an insignificant loss when the process was handled properly. Acids present, or certain alkalies to any great extent, increased the solubility of the salt so much that the loss became appreciable. Another source of error was, to Guyard's mind, loss of zinc during the ignition of the zinc ammonium phosphate with the paper on which the precipitate had been collected. Garrigues (*Journ. Am. Chem. Soc.*, xix., 936) found, in estimating zinc in a practical way, that this process advocated by Guyard gives in solutions of zinc free from salts of all metals, even alkaline salts—solutions that from previous steps in analysis, however, must have contained ammonium chloride in large amount—as satisfactory results as Guyard claimed for it. Garrigues' method of procedure was to add acid diammonium phosphate to a warm solution of zinc exactly neutralised with either hydrochloric acid or ammonia, so that the weights of zinc ammonium phosphate and that of the diammonium phosphate added should be as one to five respectively, to heat until the flocky precipitate becomes crystalline and subsides, filtering off on asbestos, drying at 100° C., and weighing preferably, although the residue may be ignited without loss, since the filtration is made on asbestos in a perforated crucible. Langmuir (*Journ. Am. Chem. Soc.*, xxi., 115) modifies the method by destroying, with dilute acetic acid, any free ammonia that may be left in the solution after boiling.

In the work that follows, in which an attempt was made to show what precipitate is formed from a solution of zinc by the action of a soluble phosphate, also what effect ammonium chloride has upon the precipitate, a solution of zinc chloride prepared as detailed below was employed. The pure zinc chloride of commerce was treated with zinc carbonate, filtered and precipitated with ammonium sulphide. This precipitate was boiled in a slight excess of hydrochloric acid until all the hydrogen sulphide was removed, and then was precipitated with sodium carbonate. After washing carefully until all the chloride was removed, the greater part of the carbonate was dissolved in sulphuric acid in slight excess, boiled with the remaining portion of the carbonate, and filtered. This solution diluted to definite volume was standardised as sulphate by evaporating the solution to dryness in a platinum crucible and heating the residue (Rose-Finkener, "Analytische Chemie," 6te Auflage, vol. ii., 117). The heating is carried on safely by so placing the platinum crucible in a radiator (consisting of a crucible and a triangle), that the bottom of the platinum crucible was held about 1 c.m. above the bottom of the outside crucible. Constant weights were obtained in successive treatment with a few drops of sulphuric acid and heating over the radiator. The results obtained in this manner were a trifle higher, though in fair agreement (when the nature of the carbonate process is taken into consideration) with determinations of the zinc in the solutions as oxide after precipitating with sodium carbonate with the usual precautions, filtering off on asbestos under pressure in a perforated platinum crucible, washing with distilled water, drying and igniting. Results are given in Table II., showing the amount of zinc sulphate found in five different portions, each of 40 c.c. of the solution of zinc sulphate, and, for comparison, the results of determinations as zinc oxide by the carbonate processes are included.

TABLE II.

$ZnSO_4$ found in 40 c.m.s of solution. Grm.	Mean value of ZnO corresponding to $ZnSO_4$ in 40 c.m.s of solution. Grm.	ZnO found in 40 c.m.s of solution by precipitation as the carbonate. Grm.
0·5386	0·2712	0·2691
0·5385		0·2685
0·5387		0·2711
0·5387		
0·5390		

Definite portions of the solution of zinc sulphate were carefully drawn from a burette into a platinum dish, heated and treated with ammonium phosphate until the solution turned red litmus paper blue. The whole was heated until the flocky precipitate became crystalline and fell to the bottom of the dish. The solution, after standing as recorded in Section A of Table III., was filtered off on asbestos under pressure in a perforated platinum crucible, and the precipitate was washed with distilled water, dried, ignited, and weighed. The filtrate in each case, as in all following cases, was tested for zinc with sulphuretted hydrogen. The results recorded in Section B of the table were obtained in the same manner as those of Section A, with microcosmic salt substituted for the ammonium salt as the precipitant. The results are below the theory for the pyrophosphate, but no appreciable amount of zinc appeared in the filtrates. Neither ammonium phosphate nor ammonium sodium phosphate seems to precipitate the ideal ammonium zinc phosphate under these conditions, and the time of standing appears to be without effect.

The results recorded in Section C were obtained by precipitating the warm solution of the zinc in presence of large amounts of ammonium chloride by adding microcosmic salt until the solution was alkaline to litmus. From these results it seems that the presence of ammonium chloride is essential for the conversion of the zinc phosphate precipitated by hydrogen sodium ammonium phosphate to the ammonium zinc salt. As a matter of fact the solutions employed by Guyard, and those in which estimations are made by practical workers, do contain ammonium chloride formed in previous steps of the analysis. The proportion of zinc to phosphate suggested by Garrigues—1 : 5—is the amount of soluble phosphate necessary to turn red litmus blue after the zinc is precipitated. In order to find out whether the presence of so large an amount of the soluble phosphate is necessary in presence of ammonium chloride, the solution of zinc sulphate was precipitated in presence of the necessary amount of ammonium chloride by the microcosmic salt, in small excess above the equivalent of the ammonium phosphate, and the solution was made just ammoniacal to litmus with a few drops of dilute ammonia, both before and after heating, to convert it to crystalline condition. Experiment (15) shows that precipitation is not complete under these conditions. The zinc left in the solution was precipitated at once as sulphide, and estimated as the oxide, after dissolving in hydrochloric acid, and precipitating with sodium carbonate. In (16) of the table the first filtrate was treated with an excess of microcosmic salt and boiled. Another portion of the ammonium zinc phosphate was precipitated, and was filtered off and estimated. No zinc was found by sulphuretted hydrogen in the second filtrate.

From the results it seems obvious also that an excess of the soluble phosphate is necessary to complete the precipitation of the zinc as the ammonium-zinc phosphate, instead of partly ammonium-zinc phosphate and partly tribasic phosphate.

In Section E of Table III. are recorded results where the precipitation was made in presence of an excess of the precipitant either alone or in presence of ammonium chloride, the solution being made faintly acid to litmus with acetic acid, according to the manner in which Langmuir recommends to conduct the precipitation. All the results by the method are low. The condition of the ammonium-zinc phosphate most nearly approximating to the ideal is obtained, as shown in 9 to 14, by precipitating in presence of ammonium chloride in large amount. Microcosmic salt is added until the solution containing the ammonium salt is alkaline, and the whole is heated until the mass subsides in crystalline condition. The amount of ammonium chloride should be 20 grms. if the filtration is to be made as soon as the solution cools. One-half the amount will do if the liquid stands a number of hours. Larger amounts tend to give a salt too rich in

ammonia. The time of standing seems to be a less important factor than either the excess of microcosmic salt or ammonium chloride.

The Ammonium-cadmium Phosphate.

According to S. Drewsen ("Gmelin-Kraut," 6te Auflage, iii., 74), the cadmium-ammonium phosphate is precipitated by allowing a solution of cadmium sulphate to stand twenty-four hours with ammonium phosphate. It is very soluble both in acids and alkalis. No further preparation of this seems to have been recorded. For the work on this salt to be given below, made with reference to determining the constitution of the salt by hydrogen-sodium-ammonium phosphate, the effect of ammonium chloride in the precipitation, and the value of the salt for quantitative work, the solution of cadmium chloride employed was prepared as follows:—A solution of cadmium sulphate acidulated with hydrochloric acid was precipitated with sulphuretted hydrogen, filtered and washed, and the precipitated sulphide was dissolved in hydrochloric acid and filtered from possible traces of copper and lead. The solution of the sulphide in hydrochloric acid was boiled until all the sulphuretted hydrogen was expelled, and filtered on asbestos in a perforated crucible of platinum under pressure. The cadmium in the filtrate precipitated with ammonium carbonate in excess was washed free from chloride, dissolved in hydrochloric acid, and diluted to definite volume. It was standardised as oxide (Browning, *Am. Journ. Sci.*, xlvi., 280) after precipitating with sodium carbonate with the necessary precautions.

The standard solution of cadmium chloride was drawn carefully from a burette into a platinum dish, and, while hot, was precipitated by adding hydrogen-sodium-ammonium phosphate until the solution was alkaline to litmus. After heating until the solution became crystalline, the whole stood three hours in case of 1 of Table IV. and sixteen hours in case of 2 and 3 before filtering. In Experiments 4 to 12 inclusive, recorded in the table, precipitation was made in the same manner as in 1 to 3 in presence of varying amounts of ammonium chloride, and the precipitates were filtered after standing as stated in Table IV. It is clear from the results that the cadmium separates out completely on long standing only. Moreover, the ideal condition of the ammonium-cadmium phosphate is obtained only when an abundance of ammonium chloride is present; but larger amounts of ammonium chloride dissolve this salt. In 14, where ammonia was added after precipitation was complete, the salt dissolved somewhat; also in 15, where the solution was left faintly acid with acetic acid, a large part of the salt was dissolved. These weights of cadmium dissolved in the filtrate were obtained by treating the filtrates with sulphuretted hydrogen, dissolving the sulphide in nitric acid, and weighing as oxide after precipitating with sodium carbonate.

The ammonium-cadmium phosphate is obtained in ideal condition by precipitating with microcosmic salt in presence of 10 grms. ammonium chloride in a total volume of 100 c.m. to 150 c.m. (shown in 6, 7, and 8, Table IV.), filtering after standing some time. On drying and igniting the pyrophosphate is left. Very large amounts of ammonium chloride (30 grms.) dissolve the salt, and seem to tend to cause the formation of a phosphate too rich in ammonia. Either acid or ammonia in small amount dissolves the salt, as is shown in 14 and 15.

The results of this investigation as to the analytical application of the double ammonium phosphates of beryllium, zinc, and cadmium may be summarised briefly as follows:—It is impossible to estimate beryllium with accuracy as the pyrophosphate obtained by igniting the double ammonium phosphate precipitated from beryllium solutions by microcosmic salt or ammonium phosphate in presence of ammonium chloride. In presence of the proper amount of ammonium chloride (10 grms. to 20 grms. in 100—200 c.m.^{3} of liquid) zinc-ammonium phosphate can be obtained in the ideal condition, which on ignition yields the pyrophosphate. This method may serve, therefore, for the accurate estimation of zinc.

Cadmium may be estimated with accuracy as the pyrophosphate if the precipitate by microcosmic salt in the nearly neutral solution containing ammonium chloride in the proportion of 10 grms. to 100 c.c. is allowed to stand several hours before filtering. In this way all cadmium separates out from the solution as a beautiful crystalline mass of cadmium-ammonium phosphate of ideal constitution. The conditions must, however, be preserved with care; there must be no excess of ammonia, no free acid, and no excess of ammonium salt beyond the quantity indicated, while that amount is necessary.

THE OCCLUSION OF HYDROGEN BY METALLIC COBALT AND OTHER METALS.*

By GREGORY PAUL BAXTER.

(Concluded from p. 296).

The Occlusion of Hydrogen by Nickel.

The study of the occlusion of hydrogen was extended to the case of a few other metals. The behaviour of nickel was found to be analogous to that of cobalt. According to Troost and Hautefeuille (*Comptes Rendus*, lxxx., 788) nickel in the form of ingots retains only traces of hydrogen, metal reduced from the oxide occludes maximum amounts and is pyrophoric, while electrolytic foil occupies a position between the two. The amount of occluded gas, according to their results, was equal in quantity to that obtained from cobalt, 100 volumes in the case of metal reduced from the oxide. Raoult (*Jahresb.*, 1869, 272) states that very porous nickel, if used as the negative pole of a voltameter, takes up 165 volumes of hydrogen, the greater part of which is given off at ordinary temperatures in the air. These high results are contradicted by those of Neumann and Streintz (*Monatsh. Chem.*, xii., 642), who found about 17 volumes of gas in metal reduced from the oxide, and by those of Richards and Cushman (*Proc. Am. Acad.*, xxxiv., 333), who found only 8 volumes in the purest metal obtained from the same source.

The lesser values are supported by the following analyses performed with material kindly furnished by Dr. Cushman, and known to be free from every impurity. In Analyses I. and II. the nickel was subjected to combustion immediately after reduction. The oxide from Analysis I. was reduced, and the resulting metal evolved no hydrogen in a vacuum, as was shown by the water yielded upon subsequent oxidation (Analyses III. and IV.). When heated in a vacuum the metal lost nearly all its occluded hydrogen (Analysis V.). Like cobalt, nickel which had been heated to a high temperature during reduction sintered together and lost its power to occlude (Analysis VI.). Finally, material reduced from the bromide occludes no hydrogen (Analysis VII.), as has already been shown by Richards and Cushman (*Proc. Amer. Acad.*, xxxiv., 333).

I. 5·7 grms. of nickel yielded 0·0033 grm. of water, or 5·7 volumes of hydrogen.

II. 4·0 grms. of nickel yielded 0·0010 grm. of water, or 2·1 volumes of hydrogen.

III. 5·7 grms. of nickel yielded 0·0060 grm. of water, or 10·7 volumes of hydrogen.

IV. 5·7 grms. of nickel yielded 0·0057 grm. of water, or 10·2 volumes of hydrogen.

V. 5·7 grms. of nickel yielded 0·0017 grm. of water, or 2·9 volumes of hydrogen.

VI. 6·0 grms. of nickel yielded 0·0006 grm. of water, or 1·0 volume of hydrogen.

VII. 1·5 grms. of nickel yielded 0·0001 grm. of water, or 0·7 volume of hydrogen.

* Contributions from the Chemical Laboratory of Harvard College. From the *American Chemical Journal*, Vol. xxii., No. 5, Nov., 1899.

Manifestly nickel is subject to the same influences as cobalt. The large amounts of hydrogen obtained by other experimenters can be explained by the fact that their material was very impure. Impure nickel and cobalt in the same state of minute subdivision apparently possess the property of retaining hydrogen to the same degree. Pure nickel, owing to its lower melting-point, should sinter more readily than pure cobalt. The lesser relative surface thus offered is probably the reason for the smaller amounts of occluded gas.

The Occlusion of Hydrogen by Copper.

The occlusion of hydrogen by copper has already been the subject of numerous researches which gave widely varying results (Graham, *Jahresb.*, 1866, 50; Thudichum and Hake, *Journ. Chem. Soc.*, 1876, xxxiii. [2], 251; Johnson, *Journ. Chem. Soc.*, xxxv., 235; Neumann and Streintz, *Monatsh. Chem.*, xii., 642; Richards, *Proc. Am. Acad.*, xxvi., 292; and others). One main fact stands out in all these investigations. Where the copper was known to be pure the occlusion was very slight, whatever the source of the copper.

Very pure cupric oxide, made by evaporation of a solution of electrolytic copper in pure nitric acid, and ignition of the residue, after reduction, yielded a very small amount of water (Analyses I., II., III., and IV.). In a vacuum at ordinary temperatures the hydrogen was retained (Analysis V.), but after ignition in a vacuum a negligible amount of water was found (Analysis VI.).

I. 2·5 grms. of copper yielded 0·0003 grm. of water, or 1·5 volumes of hydrogen.

II. 5·1 grms. of copper yielded 0·0009 grm. of water, or 2·1 volumes of hydrogen.

III. 5·1 grms. of copper yielded 0·0010 grm. of water, or 2·3 volumes of hydrogen.

IV. 5·1 grms. of copper yielded 0·0009 grm. of water, or 2·1 volumes of hydrogen.

V. 5·1 grms. of copper yielded 0·0008 grm. of water, or 1·8 volumes of hydrogen.

VI. 5·1 grms. of copper yielded 0·0003 grm. of water, or 0·7 volume of hydrogen.

The Occlusion of Hydrogen by Silver.

Silver reduced from the oxide takes up minimum amounts of hydrogen, if any.

I. 2·5 grms. of silver yielded 0·0001 grm. of water, or 0·5 volume of hydrogen.

II. 2·5 grms. of silver yielded 0·0005 grm. of water, or 2·8 volumes of hydrogen.

III. 5·0 grms. of silver yielded 0·0003 grm. of water, or 0·8 volume of hydrogen.

This result is in accordance with the results of Graham (*Jahresb.*, 1866, 51), whose silver wire occluded 0·2 its volume of the gas, while his metal, obtained by reduction of the oxide, yielded 0·9 its volume. Neumann and Streintz found no hydrogen in their silver reduced from the oxide (*Monatsh. Chem.*, xii., 642).

It is noteworthy that in all the work performed upon the occlusion of hydrogen by the four metals, cobalt, nickel, copper, and silver, when they were reduced from pure oxides at low temperatures, the magnitude of the occlusion varied with the fusion-points of the metals. Cobalt, whose melting-point is the highest, occludes by far the greatest volume of gas, while silver, which melts at the lowest temperature, occludes minimum quantities. The explanation of this peculiarity has already been mentioned. The sintering or fusing together of the metals is greater, the nearer the reduction temperature is to their melting-points, while the surface offered, which determines the amount of occlusion, diminishes with the amount of sintering. Since the melting-points of copper and silver are very near together, one would expect their power of occlusion to be very nearly the same, as is the case.

Pure ferric oxide is not reduced to any considerable extent by hydrogen at the low temperature employed in the case of the four preceding metals. When a temperature sufficiently high to produce reduction is employed, no appreciable amounts of hydrogen are occluded, because of sintering of the metal. On account of this difficulty no work could be done with iron which would be comparable with that done with the other metals.

The question as to the formation of compounds of the metals with hydrogen, similar to "Hydrogenium," is not easily settled. On the one hand, the fact that the quantity of occluded gas varies with the surface presented seems to point to simple condensation on the surface, as in the case of charcoal; on the other hand, the pertinacity with which the hydrogen is retained in a vacuum when cold is evidence in the other direction. For the present this point must needs remain undecided.

A word can be profitably said here in regard to the use of the terms "occlusion" and "adsorption." In its stricter sense the word "occlusion" should be confined to an intimate combination, such as that of palladium with hydrogen. "Adsorption," on the other hand, refers to simple condensation or concentration in the immediate vicinity of a given surface. Owing to the doubt as to the nature of the process by which the hydrogen is retained by the metals considered, the question as to the designation of the process is necessarily unsettled, but Graham's word has been usually employed above.

In conclusion, I wish to express my thanks to Professor Theodore William Richards for much advice and encouragement given during the course of this work.

DIRECTIONS FOR CERTAIN ALKALOIDAL ASSAYS.

By H. M. GORDIN and A. B. PRESCOTT.*

A General Method for the Extraction of Alkaloids in Assays.

(Note.—Analytical results in support of these directions are given in an accompanying paper, "Further Work upon the Estimation of Alkaloids and the Assay of Alkaloidal Drugs," presented in this Association at this date. Also in the paper entitled, "Certain Alkaloidal Periodides, and the Volumetric Estimation of Alkaloids as Higher Periodides," by the same authors, *Proc. Am. Phar. Assoc.*, 1898, p. 340; *Pharm. Arch.*, I. p. 121; *Journ. Am. Chem. Soc.*, 1898, p. 724. A paper on Hydrastine Hexiodide and Assay of Hydrastis, *Am. Journ. Pharm.*, 1899, p. 257. Further, see the article, "The Periodides of the Alkaloids as Molecular Forms for Estimation," &c., by A. B. Prescott, 1897, *Pharm. Review*, vol. xv., and other papers since 1895).

I.—As a Method by Percolation.†

One to four grms. of the finely powdered drug is weighed into a low wide-mouthed vessel, with a round bottom, holding eight or ten ounces, and having a well-fitted cork, such as a screw-top ointment jar (an ordinary tea cup fitted with a specie cork answers well). The powder is rubbed up with a small pestle to a fine paste by adding a little of a solvent mixture, composed of stronger ammonia water and alcohol, each 5 c.c., chloroform 10 c.c., and ether 20 c.c.‡ Then a few more c.c. of this mixture are added, so as to have the drug well covered with the liquid, using in all about five times the amount of the drug taken. The vessel is corked, with the pestle inside, and is set aside for about four or five hours, taking care to agitate by circular movement very frequently during that interval.

* In the Work of Research Committee D., Section 2, Committee on Revision and Publication of the Pharmacopœia of the United States, 1890—1900. Read before the American Pharmaceutical Association, September, 1899.

† These directions were published, nearly as here given, by the authors, in an article, "Emetine Octoiodide," &c., *Pharm. Review*, vol. xvii., 1899. This general method is not applicable to ipecacuanha. See under "Assay of Ipecacuanha" further on.

‡ In the case of Hydrastis canadensis the chloroform is replaced by an equal volume of ether.

After that time the cover is removed, and the vessel kept in a current of air, stirring frequently till all odour of ammonia has disappeared. With a good draught and frequent stirring the powder will be almost perfectly dry in about one hour. The vessel is then put into a vacuum desiccator over sulphuric acid for about four or five hours.

An amount of powdered sodium chloride,* equal to about five or six times the amount of drug employed, is then carefully mixed in, with use of the pestle, and the whole thrown into a small percolator, one provided with a glass stop-cock, and having a plug of cotton at the bottom. (A suitable percolator is easily made out of an ordinary piece of glass tubing fitted with a perforated cork, through which passes a tube having a glass stop-cock).

The vessel is then cleaned out several times with small quantities of sodium chloride, and the cleanings added to the percolator. The mixture in the percolator is then covered with a little of the cotton, which is pressed down with a piece of glass, and a suitable menstruum, usually chloroform, is poured slowly into the percolator till the menstruum reaches the stop-cock. The latter is then closed, the percolator covered and set aside for five or six hours. After that time the stop-cock is opened, and the drug exhausted with the menstruum, percolating until ten drops of the percolate being evaporated on a watch-glass, and the residue taken up with a few drops of acidulated water, the solution shows no turbidity whatever on adding a few drops of the solution of iodine. When finished, the percolate, which is received in a flat evaporating dish, is placed in a good draught at a temperature of about 30° C. When the liquid is reduced to a very small volume 10 c.c. of acidulated water† are added, and then a few c.c. of ether, or petroleum ether, so as to have an ethereal liquid cover the aqueous solution,‡ when the whole is stirred with a glass rod until all the ethereal liquid is driven off. The liquid is then filtered, and the evaporating dish and filter washed several times with acidulated water. In this way is obtained a colourless solution of the alkaloid, which can be worked up for any method of estimation.§

II.—As a Hot Extraction Method.

Instead of the cold percolation, as above directed, hot extraction in any suitable apparatus may be used, all other features of the operation being the same. If a Soxhlet tube is used care should be taken that the syphon works intermittently, as otherwise the extraction is very incomplete; if Dunstan and Short's apparatus (*Pharm. Journ.* [3], xiii., 664) is used, the boiling of the solvent should be so regulated as to have always a layer of about 2 c.m. of it on the top of the drug. Our experience has taught us that for quantitative work cold extraction by percolation requires less skill and care than hot extraction in a Soxhlet tube, though with careful operation the latter method is preferable.

The Volumetric Estimation of Alkaloids by Precipitation with Free Iodine.‖

Estimation by Formation of a Periodide, so far Applied to Atropine, Morphine, Strychnine, Brucine, Emetine, Hydrastine, and Caffeine.

For opium assay see *prox.*

For assay of nux vomica, with separation of strychnine from brucine, see *prox.*

For assay of ipecac., see *prox.*

For estimation of berberine in assay of hydrastine, see *prox.*

For estimation of caffeine the alkaloidal solution must be invariably acidulated (Gomberg, 1896). For assay of kola, see Knox and Prescott, 1896-7, *Proc. Am. Phar. Assoc.*, xliv., p. 128, and xlv., p. 131; *Journ. Am. Chem. Soc.*, xix., p. 63; xx., p. 34.

The Reagents and Utensils Required in the Volumetric Work.

(1) A standardised solution of iodine dissolved in water with iodide of potassium to be of about decinormal strength (12·653 grms. of free iodine in 1000 c.c.). The solution may be made as the volumetric test solution of iodine of the U.S.P., and used with the exact decinormal factor of iodine if preferred.

(2) A solution of sodium thiosulphate, of about decinormal strength, standardised to known ratio with the iodine solution. The volumetric test solution of thiosulphate of the U.S.P. may be used.

(3) The starch test solution of the pharmacopœia.

(4) The burettes and centesimal measuring vessels for any volumetric work in analysis.

The Volumetric Operation.

The final alkaloidal solution obtained by whatever mode of extraction,* but always representing a definite quantity of the drug to be assayed, is poured slowly and with constant stirring into a flask holding 100 c c., in which has been previously drawn 20 or 30 c.c. of the standardised solution of iodine, and 1 or 2 c.c. of dilute hydrochloric acid† (U.S.P.). The flask is then filled up to 100 c.c., stoppered, and well shaken till the periodide has separated out. The supernatant liquid is to be perfectly transparent, but of a red iodine colour. Fifty c.c. are then filtered off, and in this portion the excess of iodine determined by means of standard sodium thiosulphate. The amount of iodine consumed, multiplied by the proper factor, gives the amount of alkaloid present in the quantity of drug taken. (For example: If operating upon 2 grms. of powdered ipecac. root, the iodine consumed be 0·957764, then the *percentage* of emetine in the drug equals $0{\cdot}957764 \times 0{\cdot}55 \times 100/2 = 2{\cdot}63$).

In case more than one alkaloid be present in the drug a *mean iodometric* factor can be drawn, as shown for strychnine and brucine in the list of factors. In alkalimetric estimations a mean factor is often used in assay for total alkaloids, and the same is equally justifiable in iodometric work when the data are known.

Should there be no precipitate with iodine, but only a slight turbidity, then the drug is extremely poor, and for the assay a much larger quantity than has been used should be taken. On the other hand, should the supernatant liquid, after adding the alkaloidal solution to the solution of iodine, and separating the periodide by shaking, have very little colour, or be almost colourless, then it is certain that the drug is very rich, and either a smaller quantity of the drug or a larger quantity of the iodine solution must be employed in the assay.

Generally, if the drug contains as much as 3 per cent of alkaloid 1 grm. should be taken for the assay; if it contains less than the above amount, but not less than two-tenths of 1 per cent of alkaloid, then a quantity between 1 and 5 grms. should be taken.

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* In the case of hydrastis the sodium chloride is replaced by barium nitrate.

† If an alkalimetric assay is intended, the acidulated water in the operation should be closely standardised and taken in definite quantities.

‡ If the menstruum is all evaporated off it is sometimes difficult to dissolve out the alkaloids with the acidulated water. If chloroform be used, coming below the aqueous layer, it evaporates too slowly.

§ The method of extraction described above presents particular advantage in those cases where several alkaloids soluble in different menstrua are present in the drug, as by using these menstrua successively a separation of the alkaloids can be easily effected. This principle we have applied to the assay of opium, and to that of Hydrastis canadensis.

‖ These directions were given in substance in an article entitled "Emetine Octoiodide and the Estimation of Alkaloids Generally," by the authors of this paper, in *Journ. Am. Chem. Soc.*, xxi., p. 234, March, 1899; *Pharm. Review*, vol. xvii., 1899.

* Directions for extraction are given further on. Other procedure for extraction is given in Lyons' "Handbook of Assaying," 1899, Detroit. Nelson, Baker, and Co., pp. 26—30.

† It is always to be remembered that this estimation by formation of *higher* periodides requires the alkaloid to be added slowly *to* the iodine with excess of the latter. Except in the case of morphine an excess of acid is not hurtful, and even promotes the separation of the periodide. Hydrochloric is to be preferred to sulphuric acid.

The Iodine Factors.

The precipitate formed.	Quantity of alkaloid to 1·0000 of iodine consumed.	Quantity of alkaloid to 1 c.c. of tenth-normal solution of iodine.(*a*)
Atropine, $C_{17}H_{23}NO_3 \cdot HI \cdot I_8$ ..	0·285	0·00361
Morphine, $C_{17}H_{19}NO_3 \cdot HI \cdot I_3$ ..	0·749	0·00948
Strychnine, $C_{21}H_{22}N_2O_2 \cdot HI \cdot I_6$	0·439	0·00556
Brucine, $C_{23}H_{26}N_2O_4 \cdot HI \cdot I_6$ ..	0·518	0·00655
Mean of strychnine and brucine	0·478	0·00605
Emetine,(*b*) $C_{28}H_{40}N_2O_5 \cdot HI \cdot I_7$	0·55	0·006
Hydrastine, $C_{21}H_{21}NO_6 \cdot HI \cdot I_5$	0·604	0·00764
Caffeine, $C_8H_{10}N_4O_2 \cdot HI \cdot I_4$ ..	0·383	0·00485

(*a*) If the analyst prefers to standardise his volumetric solution of iodine to exact decinormal strength, or to adjust the consumption of iodine to this strength by use of a correcting factor, then he will multiply the c.c. of iodine solution consumed by the proper factor in this column. (1 c.c. decinormal solution contains 0·012653 grm. of iodine). The more simple way, however, is to register the actual quantity of iodine in 1 c.c. of the solution, be the same above or below the 0·012653 grm., and multiply this actual quantity by the number of c.c. used up, so as to get the *weight* of iodine consumed. This, multiplied by a factor of the first column above, gives the quantity of alkaloid estimated in grammes.

(*b*) That is a provisional representative of the total alkaloids of ipecacuanha.

The Assay of Opium.

The Extraction of the Morphine and its Volumetric Estimation either by Standardised Solution of Acid or by Standardised Solution of Iodine.

(This method of assay with the iodometric estimation appeared in its primary form, with the analysis of morphine tetraiodide, &c., in an article by the present authors, in June, 1898 (*Pharm. Archives*, i., p. 121), and with some additions in *Proc. Am. Pharm. Assoc.*, 1898, p. 340; also in *Journ. Am. Chem. Soc.*, 1898, p. 724. The directions, with adaptation to the alkalimetric way of estimation, as here given, formed a part of "The Assay of Opium: a Supplementary Note" in the *Pharmaceutical Review*, xvii., 1899, and to appear in the *Archiv der Pharmacie*).

For the use of *hot extraction instead of cold percolation* in treatment of the opium in this process, see an article entitled "Further Work upon the Estimation of Alkaloids," in which also are included a few results in comparison with the U.S.P. method, and a brief discussion of the subject.

The Materials and Utensils for the Assay.

Opium in very fine powder. Powdered sodium chloride, such as is used for the table. An ethereo-ammoniacal mixture composed of stronger ammonia water (U.S.P.) and alcohol, of each 5 c.c.; chloroform (U.S.P.), 10 c.c.; and ether, 20 c.c. Benzol boiling at about 80° C. A mixture of one volume of absolute alcohol and five volumes of chloroform. Twentieth normal sulphuric acid and twentieth normal potassium hydrate solution. Neutral methyl-orange paper. Standard solution of iodine, of any known strength in the neighbourhood of 1 per cent, and standard solution of sodium thiosulphate of about twentieth normal strength.

A 4 or 6 ounce screw-top ointment jar, having a bottom concave within. A small pestle, just long enough to rest half upright within the jar when it is closed. A small glass percolator provided with a stopcock, and of the length of about 22 c.m. and inner diameter of about 1·3 c.m. (the lower part of a burette cut in two answers very well).

Directions for the Assay.

Weigh out 3 grms. of the opium into the ointment jar, rub it up by means of the pestle with a few c.c. of the ethereo-ammoniacal mixture to make a fine paste, taking care not to smear the sides of the jar unnecessarily, then add about 2 c.c. more of the same mixture, so as to have the opium well covered with liquid, screw down the top, leaving the pestle inside, and set the jar aside for five or six hours. After that time the jar is opened, about 10 grms. of the sodium chloride thoroughly mixed in with the opium, and the open jar placed in a good current of air, stirring frequently with the pestle in order to prevent formation of lumps. In about an hour the powder will be nearly dry. The jar is then placed in a vacuum desiccator containing, besides sulphuric acid, a vessel of paraffin, and left there over night. The jar is then taken out, any lumps in the powder carefully crushed with the pestle, and the mixture transferred first to the glazed paper, and then to the percolator, in the bottom of which a plug of cotton has been placed. The jar is rubbed out several times with small quantities of the sodium chloride, the rinsings added to the percolator, and, having placed a plug of cotton and a piece of glass on the top of the powder, the opium is extracted with benzol by percolating very slowly, until, upon evaporating ten drops of the percolate on a watch-glass, and taking up the residue with ten or twelve drops of very slightly acidulated water, no turbidity appears by the addition of two drops of the iodine test solution. After the narcotine, thebaine, codeine, and most other alkaloids have in this way been completely removed by the benzol, the receiver is taken away (the benzol, of course, can be recovered by distillation, and used over and over again), and a shallow evaporating dish placed under the percolator.

The percolation is now continued slowly with the mixture of alcohol and chloroform (see Burg., *Zeit. Anal. Chem.*, xix., p. 222) until ten drops of the percolate tested as above give no reaction for alkaloids. The evaporating dish is now put into a good current of air and left over night, or until the solvent has disappeared. (This makes the whole assay occupy about two days and two hours if it be started in the morning). The bottom of the dish will then be found to be covered with a good crop of crystals intermixed with a little resinous matter.

Estimating in the Alkalimetric Way.

Fifty c.c. of the twentieth normal sulphuric acid are now carefully run out from a burette into the evaporating dish, the contents rubbed well with a pestle till everything is detached from the bottom and sides of the dish, and then, without filtering, poured into a tall narrow measuring cylinder. The dish is then carefully washed several times with small quantities of water, the washings added to the cylinder, and the latter filled up to make 90 c.c. After shaking well a few minutes, and setting aside till solid particles have settled down (the filtration is much accelerated if the waxy particles are prevented from entering the filter), 75 c.c., representing 2½ grms. of the opium, are filtered off into a beaker holding some 250 or 300 c.c., about 50 c.c. of water added, and then 35 or 40 c.c. of the twentieth normal potassium hydrate run out from a burette into the beaker. Twentieth normal sulphuric acid is now carefully added, 1 c.c. at a time, stirring with a glass rod, and testing the liquid after each addition by immersing for about fifteen seconds small strips of neutral methyl-orange paper. As soon as the paper becomes reddish, 1 c.c. of the potassium hydrate solution is added, and then again of the sulphuric acid, adding now one-tenth of a c.c. of the latter at a time, till the paper becomes reddish. In order to get exact results, the acid and alkali solutions should be standardised in nearly the same conditions under which the titration of morphine takes place; that is, using about 175 c.c. of liquid, and noting the appearance of the reddish tint upon the test-paper at the point of neutrality. The strips of reagent paper should, of course, be wet with the wash-bottle before immersion in the beaker. Though the solution of morphine has a yellow colour from some extractive matter, so that the end reaction cannot be found by adding a liquid indicator to the solution, there is not the slightest difficulty in noting

the appearance of the reddish tint upon the cream-coloured methyl-orange paper. Of course other indicators, like iodo-eosin in ethereal solution, &c., might be found to give equally good results; but having found the dip-test with methyl-orange paper to give sharp and definite results with this alkaloid, we have not experimented upon other indicators.

One c.c. of twentieth normal acid being equivalent to 0·0142 grm. anhydrous morphine, the number of c.c. of the acid consumed by the alkaloid from 2½ grms. opium, multiplied by 0·568 (=0·0142, 100/2·5), gives the percentage of morphine in the opium.

Estimating in the Iodometric Way.

When it is desirable *to control* the alkalimetric assay with an iodometric one, the contents of the beaker are emptied in a 250 c.c. measuring flask, washing the beaker two or three times with small quantities of water, the flasks filled up to 250 c.c., about 3 or 4 grms. calcium hydrate added, and the mixture shaken for about an hour. This treatment removes a good deal of the colouring matter, but keeps the morphine in solution. 50 c.c., which represent half a grm. of opium, are now filtered off into a 100 c.c. flask, and the liquid slightly acidified with hydrochloric acid. The liquid will now be only slightly coloured, 20 c.c. of the standard iodine are now run out from a burette into the flask, the latter filled up to 100 c.c., and the flask well shaken till the supernatant liquid becomes perfectly transparent, but has a dark red iodine colour.* 50 c.c. are now filtered off, and the excess of iodine determined by the standard sodium thiosulphate, using starch as indicator. The amount of iodine consumed by the half grm. of opium, multiplied by 149·8 (=0·749 × 100 × 2),† gives the percentage of morphine in the opium.

If only an iodometric assay be desired but 1 grm. opium need be taken for the assay, and the latter conducted exactly as described above up to the point where the chloroform alcohol has been removed by evaporation. At this point the residue is taken up with good lime water by rubbing the evaporating dish thoroughly with it, pouring the mixture in a 100 c.c. flask, filling the latter up with lime water to make 100 c.c,, shaking the flask about an hour, filtering off 50 c.c. into another 100 c.c. flask, acidulating, and then finishing up as above.

The Assay of Nux Vomica.‡

The acidulated water solution of the total alkaloids of the drug, as obtained by the directions on page given above, or other mode of extraction, is made up to a definite volume, say 100 c.c. If 4 grms. of the drug have been taken, then 25 c.c. will represent 1 grm. of the drug, and will be sufficient for one estimation. This volume, then, is run from a burette into a 100 c.c. flask in which has been placed 20 c.c. of the decinormal iodine solution and 2 c.c. dilute hydrochloric acid, when the amount of iodine consumed by the total alkaloids in that 1 grm. of of nux vomica is reached in the way described above. Let that amount be *a*. If only the amount of total alkaloids in the nux vomica is desired, it is sufficient to multiply *a* by 47·8, which is equal to 100 times the mean factor of strychnine and brucine, and the *percentage* of total alkaloids is at once obtained.

For the Separate Estimation of Strychine and Brucine a modification of Dunstan and Short's§ method of separation by ferrocyanide, we have found to work fairly well as follows:—Another portion of the alkaloidal solution, representing 2 grms. of the nux vomica, that is 50 c.c., is run out from the burette into an Erlenmeyer flask of the capacity of about 300 c.c., and to the contents of the flask 10 c.c. of a 2 per cent solution of sulphuric acid is added, and then water enough to make in all about 200 c.c. Then pour in 25 c.c. of a 5 per cent solution of potassium ferrocyanide, stopper the flask, and shake continuously for about half an hour. Now filter, wash the precipitate on the filter repeatedly with water containing 1 per cent of sulphuric acid till a few drops of the filtrate diluted with a little water have no bitter taste. The filter is then pierced, and the precipitate rinsed with use of the wash-bottle into a 100 c.c. flask. To the contents of the flask are then added 20 c.c. of a 5 per cent solution of zinc sulphate, and the flask kept on a boiling water-bath for about fifteen minutes. The zinc sulphate decomposes the strychnine ferrocyanide, zinc ferrocyanide is precipitated, and strychnine sulphate remains in solution. The flask is then completely cooled, and water enough added to make 100 c.c. Of this 50 c.c.—representing again 1 grm. of the nux vomica, but deprived of the brucine—are then filtered off, and run out from the burette into a 100 c.c. flask containing 20 c.c. decinormal iodine solution and about 2 c.c. of dilute hydrochloric acid. The amount of iodine consumed by the strychnine alone is then determined as above. Let it be *b*. Then $b \times 43{\cdot}9$ (100 times the strychnine factor) gives the percentage of strychnine, and $(a-b) \times 51{\cdot}8$ is the percentage of brucine in the nux vomica.

To test the exactness of this method, we prepared a solution containing known quantities of each of these alkaloids, and determined the same by the described method. The results, as can be seen from the following statement, are fairly satisfactory, if we consider the well-known difficulties of this separation. The solution contained 0·16 per cent strychnine and 0·22 per cent brucine (anhydrous).

	Iodine consumed by 10 c.c. before the removal of brucine.	Iodine consumed by 10 c.c. after the removal of brucine.	Found.		Contained.	
			Strychnine.	Brucine.	Strychnine.	Brucine
1.	0·0843132	0·032397	0·14	0·24	0·16	0·22
2.	0·0843130	0·032397	0·14	0·24	0·16	0·22

Assay of Ipecacuanha.

For extraction of the drug use one of the methods given in Lyons' "Assaying" (*Detroit*, 1899). The cold percolation process of extraction previously directed as already remarked, does not work well with this drug.

Ether, chloroform, and acetone were tried as menstrua in the cold percolation, but the results were too low. The ammoniated mixture fails to yield all the alkaloid. This possibly explains why Flückiger (*Pharm. Zeitung*, 1886, p. 30), extracting by ammoniated chloroform, obtained exceptionally low results (See also Guareschi, *Alkaloide*, 1896, p. 527).

In iodometric estimation the total acidulated alkaloid solution is made up to a definite volume, an aliquot portion taken, and added to a measured excess of the iodine solution, as directed heretofore. The iodine factor of emetine is taken as fairly near the mean factor of the total alkaloids.

Assay of Hydrastis.

In the assay of *Hydrastis canadensis*, for berberine and for hydrastine, the Directions for the Assays are given in an accompanying article entitled "Further Work upon the Estimation of Alkaloids," &c. In the plan of the assay the hydrastine is dissolved with absolute ether, and estimated iodometrically, as a hexaiodide. The berberine, undissolved by the absolute ether, is estimated volumetrically by precipitation as berberine hydriodide, the excess of the precipitant, potassium iodide, being determined by silver nitrate with sulphocyanate. But before the berberine is precipitated as hydriodide, it is separated in its acetone compound. And before the alkaloids are acted

* See our article in *J. Am. Chem. Soc.*, 1898, p. 722; *Proc. Am. Phar. Assoc.*, 1898, p. 368.

† 0·75 is here taken instead of 0·74914, which is the factor for morphine (*loc. cit.*, *p.* 724).

‡ From an article by the authors in *Pharm. Review*, xvii , 1899.

§ *Pharm. J. Trans.* (3), xiv., 290; *Am. J. Pharm.*, 1883, 579. Any other method of separation of strychnine and brucine may be used with the iodometric estimations.

upon by the reagents, they are liberated from the powdered drug by maceration with an ethereo-ammoniacal mixture.

CORRESPONDENCE.

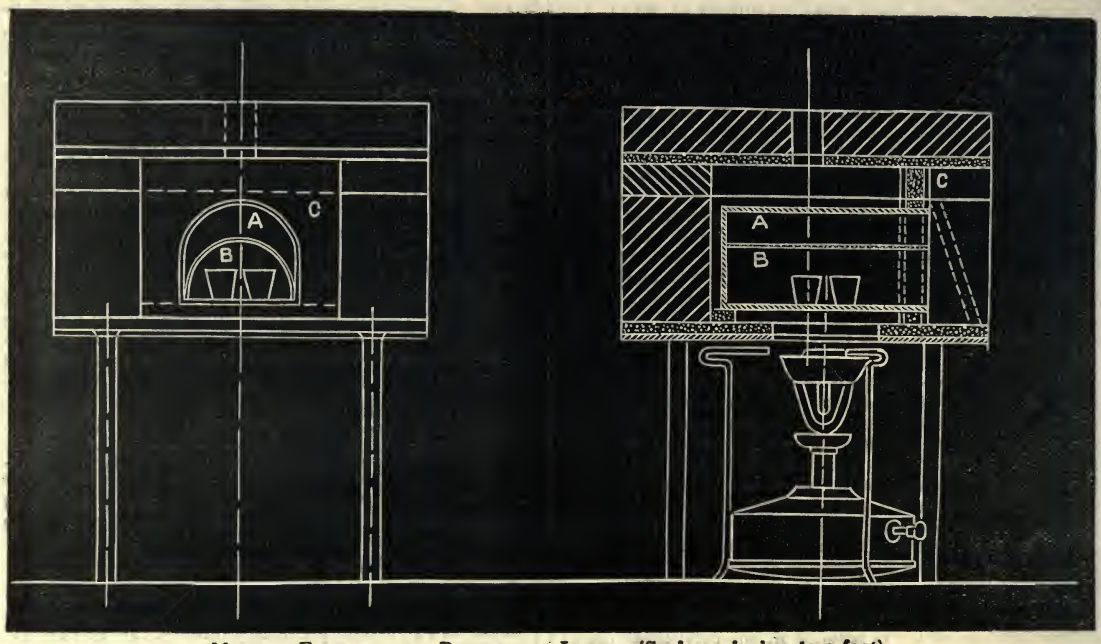
LABORATORY LAMP.

To the Editor of the Chemical News.

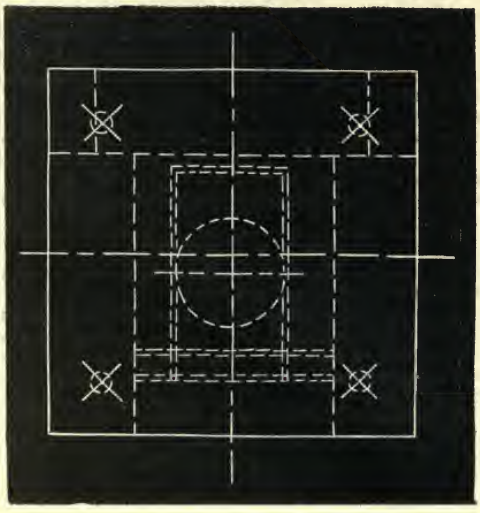
Sir,—Seeing that Prof. Frank Clowes has replied to "Chemicus," and that he suggests the use of a methylated spirit lamp arrangement, and, as this may be too expensive for him, I herewith send a drawing of my arrangement of a (Swedish) petroleum lamp, with a muffle furnace of simple construction, which I find very efficient and cheap in the determination of the ash of coal, coke, yeasts and beer, and water residues.

On lighting up lamp, and placing it in position shown under muffle, in ten minutes more than half of the bottom of muffle is heated to a red heat; on introducing four samples of about 2·5 grms. of coal in porcelain crucibles, in from ten to fifteen minutes all the volatile matter is evolved, and in three hours' time the weights of ash are constant. This is less time than I can do same quantities in a Fletcher's gas-heated muffle furnace, and only with a consumption of petroleum 0·797 at the rate of 6 ozs. by vol. per hour.

This class of lamp can be adapted to most other heat-requiring purposes (excepting combustions) that I know of in the laboratory, and it can be purchased at most lamp-shops for 12s. 6d.—I am, &c.,



Muffle Furnace for Petroleum Lamp. (Scale—2 inches to a foot).



Geo. Valentine.

Research Laboratory,
Montpelier Hill, Dublin.

RELATIONS BETWEEN THE ATOMIC WEIGHTS AND PHYSICAL PROPERTIES OF ELEMENTS.

To the Editor of the Chemical News.

Sir,—Mr. Bayley's note in your issue of the 15th inst. (Chem. News, vol. lxxx., p. 282) seems to have a defect, and that is, if the formula melting-point (absolute) × co-efficient of linear expansion gives a constant for some elements, why should it not do so for all?

To take a universal absolute zero as −273° C. can lead to many misunderstandings. That this temperature should have the properties attributed to absolute zero is, in the light of our present knowledge, impossible, and the title is only a survival from the infancy of modern chemistry.

If the two cubes of Zn and Cd, mentioned by Mr. Bayley, were of the same volume at absolute zero, they would be

of the same volume at their respective melting-points, but the absolute zero for each would differ. Therefore, in the cases given, the coefficients of expansion (taken presumably at similar temperatures) are multiplied by ranges of temperature not similar, and thus the constant obtained may be due to chance.

More likely, the coefficient of expansion, taken in each case at a temperature similarly located between the melting- and boiling-points, multiplied by the range of temperature between the melting- and boiling-points, would give a more universal constant.—I am, &c.,

ALFRED WERTHEIMER.

Stirling Chemical Works,
Stratford, E., Dec. 26, 1899.

REMINISCENCES OF BUNSEN.

To the Editor of the Chemical News.

SIR,—In Mr. Bolton's interesting Reminiscences of Bunsen (CHEMICAL NEWS, lxxx., 283), he mentions the fact of Bunsen touching a quantitative precipitate, and his washing it off Bunsen's thumb.

Forty-six years since ,I remember Dr. Medlock telling me a similar tale, the only difference being that the one who touched the precipitate, and used the same words as Bunsen, being a petty German Prince who was visiting the laboratory, and the one who used the wash-bottle being Liebig.

The Prince, I think, would be more likely to touch the precipitate than Bunsen, from the latter's instinct as a chemist, even although he may have been an "Absent-minded Beggar."—I am, &c.,

E. B.

December 19, 1899.

OBITUARY.

JOHN FREDERICK HODGES.

IT is with regret that we record the death of Prof. John Hodges, M.D., J.P., of Queen's College, Belfast, which took place on December 13th at the ripe age of eighty-four years.

The name of Prof. Hodges has been identified with Belfast for more than a generation, but the news of his death will cause a feeling of sorrow extending beyond the limits of the city in which it occurred.

John Frederick Hodges was born in County Down, and early entered the medical profession. He studied at Glasgow University, and in the year 1837 he became a Licentiate of the Faculty of Physicians and Surgeons. Shortly afterwards Dr. Hodges entered upon a general medical practice at Downpatrick. He had, however, always manifested a strong taste for chemistry, and having, while at Glasgow, come under the influence of the celebrated Graham, and also having his attention drawn to the researches of Liebig, he decided upon devoting himself entirely to the pursuit of chemical science. He therefore abandoned his practice and proceeded to Germany, where he studied at the University of Giessen. This entirely changed his subsequent career, and on his return home he devoted himself solely to chemistry, more especially in its bearing upon agriculture —a subject in which he acquired a high reputation.

Dr. Hodges succeeded Dr. Andrews as Lecturer on Chemistry in the old Belfast College, and on the foundation of the local Queen's College he was appointed Professor of Agriculture and also Lecturer on Medical Jurisprudence. He was a Fellow of a number of scientific societies, and held many appointments, besides being the author of a number of works on chemistry. He was married and had a large family, some of whom have already distinguished themselves in various fields.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 23, December 4, 1899.

Compound Metallic Radicles. Mercury Derivatives.—M. Berthelot.—The author has measured the heat of formation of three mercury-derived radicles—mercury dimethyl, mercury diethyl, and mercury diphenyl.

Lactic Acid.—MM. Berthelot and Delépine.—Lactic acid and its nitrogen and other derivatives play an essential part in all investigations relating to animal heat. Their heats of combustion and formation are imperfectly known, only having been determined by an indirect calculation and by an approximate numerical relation, deduced from numbers obtained not from the acid or its salts, but from its ether. The authors have re-determined the numbers in three different ways—by means of silver lactate, zinc lactate, and a lactide, a very important anhydride, on account of its constituting with glycolide the prototypes of the anhydride of the alcohols of the acids.

Explosion of Potassium Chlorate.—M. Berthelot.—Potassium chlorate is an endothermic compound, $KClO_3 = KCl + O_3$ (liberated) $+ 11{\cdot}9$ cal. It developes 33·5 litres of oxygen for 1 grm. However, potassium chlorate is not classed among explosive bodies, since it does not detonate under a progressive heating. The author makes a series of experiments on the conditions which cause this substance to detonate, and compares them with the conditions under which picric acid explodes.

Researches on and Estimation of very Small Quantities of Arsenic in Tissues.—Armand Gautier.—The author's method consists in destroying the organic matter successively by nitric acid and sulphuric acid, then again by nitric acid. The action from the beginning to the end takes place in the midst of strongly oxidising agents, and the whole of the chlorides are destroyed almost at the beginning, these latter being one of the principal causes of the loss of arsenic under the form of volatile compounds.

Dissociation by means of Water, of Ammonium Iodomercurate and Potassium Iodomercurate.—Maurice François.—The author's series of experiments show that the decomposition of ammonium iodomercurate, $HgI_2NH_4I.H_2O$, by small quantities of water, is limited and reversible. It obeys the laws of the dissociation of salts by water. The same is true of the decomposition of potassium iodomercurate, $HgI_2KI.5H_2O$. When the state of equilibrium is reached, the liquor contains a quantity of free NH_4I and KI, constant for a given temperature.

Heat of Fractionated Neutralisation of Carbonyl Ferrocyanhydric Acid, compared with that of Ferrocyanhydric Acid.—J. A. Muller.—The calorimetric determinations which the author makes lead to the following conclusions: —(1). Carbonyl ferrocyanhydric acid is a strong acid, in the same way as ferrocyanhydric acid, because the neutralisation of these acids by strong bases liberates, in very dilute solutions and at ordinary temperatures, about 14 calories per grm.-atom of hydrogen neutralised. (2). The heat evolved, per grm.-atom of hydrogen, in the neutralisation of carbonyl ferrocyanhydric acid by potash or by baryta, being the same, or sensibly so, as that obtained with ferrocyanhydric acid under the same conditions, it results that the substitution

in the molecule of this latter acid of a divalent CNH group by carbonyl has no sensible influence on the acid energy of the hydrogen atoms which remain in the molecule of carbonyl ferrocyanhydric acid formed.

Some New Compounds of Phosphoric Anhydride and Benzene.—H. Giran.—When benzene monodimeta-phosphoric acid is treated with solutions of soda, potash, ammonia, carbonates of sodium, potassium, &c., yellow precipitates are formed which decompose rapidly under the influence of water. These precipitates are, without doubt, the benzene monodimeta-phosphates of sodium, potassium, ammonium, &c., but it is impossible to collect them. The author has, however, prepared benzene tridimeta-phosphoric acid, which has the constitutional formula—

$$C_6H_3\begin{cases}P_2O_5H\\P_2O_5H\\P_2O_5H\end{cases}$$

from which the ammonium salt was prepared. He has also established the fact that toluene, xylene, anthracene, and other analogous carbides, unite with phosphoric acid, some even in the cold, to give compounds which appear to be of the same species as the preceding, but which will be examined further.

Preparation of Tetrachlorated and Tetrabromated Orthoquinones from corresponding Halogenated Gaïacols and Veratrols.—H. Cousin.—The result of the author's experiments on the preparation of the above compounds shows that nitric acid first saponifies the tetrachlorated and tetrabromated gaïacols and veratrols, and transforms them into substituted pyrocatechins. These are then oxidised, and give the corresponding quinones.

No. 24, December 11, 1899.

A General Method for the Estimation of some Simple Bodies contained in Organic Compounds.—M. Berthelot.—The author shows that it is possible to use a general method for estimation of simple bodies, easier and more rapid in many cases than the ordinary method, founded on the same principles as those employed for calorimetric investigations. A short account is given of the results observed in the analyses which follow the calorimetric determination. Oxygen is used compressed to 25 atmospheres in a calorimetric bomb. Carbon is thus weighed in the form of CO_2, hydrogen as water. &c.

Action of Aluminium Chloride on Camphoric Anhydride.—G. Blanc.—The action of aluminium chloride on camphoric anhydride gives, as is known already, isolauronolic acid. At the same time, during this reaction, are produced a certain number of secondary products. After the separation of isolauronolic acid, the mother-liquor is subjected to distillation under reduced pressure, when it is separated into two parts, a portion which distils over and a residue. A number of extractions with potassium bicarbonate divide the distillate into two parts, one acid and one neutral. The acid portion consists probably of a mixture of the two substances corresponding to the formulæ $C_9H_{14}O_2$ and $C_9H_{16}O_2$. The neutral portion of the distillate is composed of an oily liquid, which is most probably the lactone of an acid, $C_9H_{16}O_3$.

Alkalimetry of Amines.—A. Astruc.—The author has examined successively the alkalimetric titration of fatty and aromatic amines, using methyl orange and phenolphthalein as indicators. The two reagents employed successively enable two very different basicities to be characterised; that of the purely fatty amines, which behave as strong bases, giving results in accordance with the thermochemical numbers; those of the primary aromatic amines behave as very feeble bases, only affecting methyl orange, a result which is also in accordance with thermochemical numbers. The influence of a second aromatic radicle in a secondary aromatic amine is to make the basicity entirely disappear to both indicators.

MISCELLANEOUS

International Congress of Methods of Testing Building Materials.—It has been decided to hold an International Congress on the Methods of Testing Building Materials, in connection with the forthcoming Paris Exhibition, from July 9 to 16, 1900, in Paris. Anyone desirous of attending this Congress can obtain all information from the Secretary at the Exhibition Buildings.

MEETINGS FOR THE WEEK.

TUESDAY, Jan. 2nd. THURSDAY, 4th. SATURDAY, 6th. TUESDAY, 9th. — Royal Institution, 3. (Christmas Lectures to Young People). "On Fluids in Motion and at Rest," by Charles Vernon Boys, F.R.S. (Experimentally illustrated).

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